Persulfate-based Advanced Oxidation: Critical Assessment of Opportunities and Roadblocks

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Abstract. Reports that promote persulfate-based advanced oxidation process (AOP) as a viable alternative to hydrogen peroxide-based processes have been rapidly accumulating in recent water treatment literature. Various strategies to activate peroxide bonds in persulfate precursors have been proposed and the capacity to degrade a wide range of organic pollutants has been demonstrated. Compared to traditional AOPs in which hydroxyl radical serves as the main oxidant, persulfate-based AOPs have been claimed to involve different in-situ generated oxidants such as sulfate radical and singlet oxygen as well as non-radical oxidation pathways. However, there exist controversial observations and interpretations around some of these claims, challenging robust scientific progress of this technology toward practical use. This Critical Review comparatively examines the activation mechanisms of peroxymonosulfate and peroxydisulfate and the formation pathways of oxidizing species. Properties of the main oxidizing species are scrutinized and the role of singlet oxygen is debated. In addition, the impacts of water parameters and constituents such as pH, background organic matter, halide, phosphate, and carbonate on persulfate-driven chemistry are discussed. The opportunity for niche applications is also presented, emphasizing the need for parallel efforts to remove currently prevalent knowledge roadblocks.

Keywords: persulfate, advanced oxidation, mechanisms, water matrix effects, byproduct formation

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INTRODUCTION

Advanced oxidation processes (AOPs) employ highly reactive hydroxyl radical (•OH) to abate a wide range of organic pollutants in water with diffusion-limited kinetics. Since •OH is short-lived, it is generated in situ during ozone- and UV-based processes by activating stable precursors such as H$_2$O$_2$. Alternative AOPs utilizing peroxymonosulfate (PMS) or peroxydisulfate (PDS) (collectively referred to as persulfate; see Figure 1 for their structures) instead of H$_2$O$_2$ have emerged based on the same strategy. In sulfate radical-based AOPs (referred to herein as ‘SO$_4$$^•$-AOPs’), highly reactive, short-lived sulfate radicals (SO$_4$$^•$) are produced in situ by cleaving the peroxide bond in the persulfate molecule via energy and electron transfer reactions. Unlike H$_2$O$_2$, however, persulfate can also oxidize some organics directly, without involving radical species. In the current literature, ‘persulfate-AOPs’ refer to any physicochemical method that enhances the oxidizing capacity of persulfate regardless of involvement of radicals.

Originally introduced for soil and groundwater remediation in the late 1990s to overcome the technical limitations of H$_2$O$_2$, over the past decades, persulfate-AOPs have drawn a significant attention as a viable alternative to traditional •OH-based AOPs in water and wastewater treatment. A simple comparison of redox potentials of key radical species, i.e., E$^0$(SO$_4$$^•$/SO$_4^{2-}$) = +2.60 - +3.10 V NHE > E$^0$(•OH/OH$^-$) = +1.90 - +2.70 V NHE, initiated a lot of optimism. Other technical advantages of persulfate-AOPs over H$_2$O$_2$-AOPs that have been identified include: (i) the higher achievable radical formation yield, (ii) a wider variety of methods available to activate persulfate, (iii) less dependence of the treatment efficiency on the operational parameters (e.g., pH, initial peroxide loading, background constituents), and (iv) lower costs of storage and transportation due to the availability of persulfate salts. A recent surge in scientific publications, mostly on developing persulfate activation strategies, also reflects this optimism that currently prevails in academic research.

Gauging the true potential of this technology as a substitute for a process that is already well established in the industry requires a careful evaluation of compounding factors such as water matrix effects, byproduct formation and toxicological consequences, costs, and engineering challenges. However, conflicting views on the identity of major oxidants and the mechanisms of persulfate activation, pollutant degradation, and background constituent influence (e.g., humic substance, chloride, and bicarbonate) exist in persulfate literature. The chemistry and mechanisms are very different as compared to •OH-AOPs, despite the similarity in the concept how they were both initially designed, to an extent that some persulfate-AOPs do not carry features that distinguish AOPs from other oxidation processes (e.g., low selectivity of •OH). Such differences originate primarily from unique reactivity of PMS/PDS and the involvement of differential radical (e.g., SO$_4$$^•$) and non-radical species (e.g., singlet oxygen ($^1$O$_2$)). Accordingly, this critical review scrutinizes the chemistry involved in these processes with special attention to similarities and differences to •OH-AOPs in order to define challenges for prioritizing future studies in this field.
SULFATE RADICAL: PRODUCTION AND PROPERTIES

In situ Production by Persulfate Activation. The primarily intended goal of persulfate-AOPs is a release of a large amount of $\text{SO}_4^{\cdot-}$ by homolytically or heterolytically cleaving the peroxide bond in the persulfate molecule. In water treatment, the peroxide bond activation (Figure 1) can be achieved by an input of energy in the form of photons (UV photolysis) or heat (thermolysis). In most often adopted approaches, peroxide bond-breaking redox reactions are initiated by direct electrolysis or by reduced metals, (Fe$^0$, Co(II)), metal oxides (e.g., CuCo$_2$O$_4$, LnMnO$_3$), and some composites (e.g., Fe/Co, Co$_3$O$_4$/C$_3$N$_4$). The occurrence of $\text{SO}_4^{\cdot-}$ has been well-documented (e.g., emergence of the maximum transient absorption at 450 nm with a molar extinction coefficient of $460 \pm 25 \text{ M}^{-1}\text{cm}^{-1}$). Its role in pollutant oxidation is also well-established based on observations such as (i) delayed pollutant degradation by addition of radical scavengers, (ii) formation of halogen-containing products (e.g., chlorinated phenols and BrO$_3^{\cdot-}$) in the presence of excess halide ions, (iii) electron paramagnetic resonance (EPR) detection of radical adducts, and (iv) product distribution and substrate-specificity that align well with the reactivity of $\text{SO}_4^{\cdot-}$. $\text{SO}_4^{\cdot-}$ can rapidly oxidize a range of organic pollutants, even leading to mineralization of select compounds upon extensive exposure. But both ‘the range of target pollutants’ and ‘mineralization potential’ need to be advocated with caution. Although the oxidation potential of $\text{SO}_4^{\cdot-}$ is comparable to that of $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$-driven oxidation is much more selective. Therefore, simply comparing the oxidation potential of $\text{SO}_4^{\cdot-}$ versus $\cdot\text{OH}$ to promote the $\text{SO}_4^{\cdot-}$-AOP is unjustified. Considering that the AOP is often synonymously taken as broadband abatement of organic compounds due to its root in less selective $\cdot\text{OH}$-based processes, this distinction is significant. The selectivity of $\text{SO}_4^{\cdot-}$ explains why it is used for persulfate-mediated organic synthesis (e.g., free radical pathway for hydroxylation of aromatics) instead of other oxidants. Below we examine both similarities and differences between $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ that are critical to water treatment applications.

Substrate Specific Reactivity. Organic compounds react with $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ via similar pathways; (i) hydrogen abstraction, (ii) electron transfer, and (iii) addition-elimination. The difference lies in a preferred reaction pathway and the reaction kinetics. For example, the oxidation of saturated hydrocarbons such as alkanes and aliphatic alcohols by $\text{SO}_4^{\cdot-}$ is known to proceed through hydrogen abstraction similar to $\cdot\text{OH}$. This is supported by the substantial kinetic isotope effect observed in oxidation of deuterated compounds. However, second-order rate constants for the reactions of $\text{SO}_4^{\cdot-}$ with typical alkanes (e.g., ethane and propane) and aliphatic alcohols (e.g., methanol and ethanol) are two or three orders of magnitude smaller than those for $\cdot\text{OH}$. Furthermore, the rate of hydrogen abstraction by $\text{SO}_4^{\cdot-}$ varies by one or two orders of magnitude depending on the degree of alkylation and the type of functional groups. This is in
marked contrast to the reactivity of *OH which is less sensitive to chemical surroundings. For instance, the second order rate constant for hydrogen abstraction by SO$_4^{\cdot}$ drastically increases with the increasing alkyl chain length; $k$(ethane) = 5.6 × 10$^6$ M$^{-1}$s$^{-1}$, $k$(propane) = 4.7 × 10$^7$ M$^{-1}$s$^{-1}$, and $k$(2-methylpropane) = 9.9 × 10$^7$ M$^{-1}$s$^{-1}$. Likewise, electron-donating groups such as alkyl, allyl, and hydroxyl moieties make the α hydrogen more susceptible to abstraction by SO$_4^{\cdot}$; $k$(1-propanol) = 5.9 × 10$^7$ M$^{-1}$s$^{-1}$, $k$(2-methyl-1-propanol) = 1.3 × 10$^8$ M$^{-1}$s$^{-1}$, and $k$(2-propen-1-ol) = 1.4 × 10$^9$ M$^{-1}$s$^{-1}$. In contrast to SO$_4^{\cdot}$, the second order rate constants for the corresponding reactions with *OH only range from 2.8 × 10$^9$ M$^{-1}$s$^{-1}$ to 3.4 × 10$^{10}$ M$^{-1}$s$^{-1}$.

The difference in reaction mechanisms for SO$_4^{\cdot}$ and *OH is quite evident when the routes of reactions with aliphatic carboxylic acids are compared (Figure 2). The first step of *OH-induced oxidation is predominantly hydrogen abstraction from carbons in the aliphatic chain attached to the carboxyl group, thus producing carbon-centered radicals, which react further by oxygen addition and then to various products according to the Russel- or Bennett-type reactions. In contrast, SO$_4^{\cdot}$ preferentially abstracts an electron from oxygen in the carboxyl group. A resulting carboxyl radical (RCO$_2^{\cdot}$) releases CO$_2$ and an alkyl radical. The decarboxylation is unique to SO$_4^{\cdot}$ (e.g., mineralization of acetic acid to CO$_2$ involving few intermediates) and distinguishes SO$_4^{\cdot}$-AOPs from *OH-AOPs with respect to the product distribution. Aromatic carboxylic acids also undergo decarboxylation by SO$_4^{\cdot}$ that proceeds sequentially through (i) formation of an aromatic radical cation through direct electron abstraction and (ii) CO$_2$ loss accompanying (substituted) an aryl radical release (Figure 2). Select aromatic carboxylic acids such as benzoic and phthalic acids decarboxylate in SO$_4^{\cdot}$-AOPs whereas hydroxylation is more common in conventional *OH-mediated AOPs.

Electron abstraction and addition-elimination mechanisms are also important routes of reactions between SO$_4^{\cdot}$ and aromatic compounds. Short-lived intermediates after electron abstraction, observed by EPR or transient absorption spectra, include (i) radical cations, (ii) SO$_4^{\cdot}$ adducts, or (iii) *OH adducts. Hydroxycyclohexadienyl-type radicals (i.e., *OH adduct), found typically after the electrophilic addition of *OH to aromatic rings, also result from either a hydration of the radical cation or SO$_4^{\cdot}$ addition followed by elimination. The selective nature of SO$_4^{\cdot}$ makes the reactivity toward aromatic compounds highly sensitive to substituent effects. This is obvious from Hammett-type correlations of SO$_4^{\cdot}$ and *OH; $\rho = -2.4$ for SO$_4^{\cdot}$ and $\rho = -0.5$ for *OH were determined from linear correlations of the logarithm of the relative second order rate constants with Hammett substituent constant ($\log(k/k_0) = \rho \sigma$ where $k$ = second-order rate constant for benzene; $k_0$ = second-order rate constant for substituted benzene; and $\sigma$ = Hammett substituent constant). Depending on the type of substituents, reaction pathway and products after the initial attack by SO$_4^{\cdot}$ also vary significantly. Long-lived aromatic radical cations due to electron-donating groups tend to rearrange to undergo side chain oxidation. For instance, a radical cation generated during p-toluic acid (or gallic acid (trihydroxybenzoic acid)) oxidation by SO$_4^{\cdot}$
rearranges to the corresponding benzyl radical (or phenoxy radical), which further converts to benzyl alcohol (or biphenyl). Dimers and trimers formed from phenoxy radicals are also characteristic products of SO\textsubscript{4}**-AOPs. Such products are barely observed in *OH-AOPs. Haloaromatic radical cations destabilized by electron-withdrawing groups (e.g., carboxylic group in p-bromobenzoic acid) are dehalogenated after rapid hydrolysis. In contrast, stable radical cations substituted with electron-donating groups (e.g., hydroxyl group in p-bromophenol) are not prone to hydrolysis, thus slowing down the dehalogenation kinetics.

**SULFATE RADICAL AND PERSULFATE: MATRIX EFFECTS**

**Interaction with Dissolved Organic Matter.** A significant decrease in the treatment efficiency due to reactions of *OH by background organic constituents such as natural organic matter (NOM) and effluent organic matter (EfOM) is a well-recognized drawback of *OH-AOPs. The SO\textsubscript{4}**-AOP is not an exception (Figure 3a), but the efficiency loss occurs generally to a much smaller extent compared to *OH-AOPs. Several studies suggested that the gross second order rate constants for the reactions between SO\textsubscript{4}** and NOM ranges from 2.5 × 10\textsuperscript{7} M\textsuperscript{-1}s\textsuperscript{-1} to 8.1 × 10\textsuperscript{7} M\textsuperscript{-1}s\textsuperscript{-1}, which is around one order of magnitude lower than for *OH (k = 1.6-3.3 × 10\textsuperscript{8} M\textsuperscript{-1}s\textsuperscript{-1}).

The kinetic inhibition by the organic matrix components depends on the extent of oxidation of the fast reacting moieties by the substrate-specific SO\textsubscript{4}**. In contrast, the inhibitory effects persist for the less selective *OH until the NOM or EfOM is almost completely mineralized. It is noteworthy that the SO\textsubscript{4}**-AOP can also be affected by more significant inhibition in some cases. For instance, degradation of organics that are less reactive with SO\textsubscript{4}** (e.g., ibuprofen or perfluorooctanoic acid (PFOA)) were found to be significantly inhibited when humic-like substances (containing aromatic and olefinic moieties that more readily scavenge SO\textsubscript{4}** than aliphatic components) are present.

In addition to being a scavenger of SO\textsubscript{4}**, some functional groups present in NOM can serve as activators for PMS and PDS (Figure 3a). For example, quinone-type compounds (e.g., p-benzoquinone) accelerates the self-decay of PMS, yielding \( \mathrm{^1O_2} \) as reactive transient intermediate. The non-radical PMS activation occurs predominantly in the basic pH region since PMS self-decomposes when the pH exceeds the \( pK_a \) value of PMS (~9.3). In contrast, PDS can undergo reductive transformation into SO\textsubscript{4}** by a semiquinone radical that forms via the comproportionation between benzoquinone and hydroquinone. Similarly, the phenolate anion, a dominant species at pH > \( pK_a \) (~10), activates PDS to SO\textsubscript{4}**, whereas the neutral phenol barely activates PDS. Some quinone and phenol derivatives with relatively low \( pK_a \) values (e.g., pentachlorophenol; \( pK_a = 4.70 \)) can activate PDS even under mildly acidic and neutral conditions. The overall oxidizing capacity of reactive intermediates such as SO\textsubscript{4}** and \( \mathrm{^1O_2} \) resulting from NOM-induced persulfate activation is marginal due to the capacity of NOM as a natural sink for reactive oxidizing species.
**Interaction with Halide Ions.** Radical scavenging by Cl\(^-\) and consequential loss of the process efficiency are a unique challenge encountered in SO\(_4^{2-}\)-AOP (Figure 3b). In conventional AOP, *OH adds to Cl\(^-\) to form ClOH\(^*\), but it mostly reverts to *OH under neutral conditions (Cl\(^-\) + OH\(^*\) \overset{\text{ClOH\(^*\)}}{\text{⇌}}\text{Cl}^\bullet + \text{H}_2\text{O})\(^{70}\). In contrast, SO\(_4^{2-}\) produces Cl\(^\bullet\) through one-electron abstraction from Cl\(^-\) (SO\(_4^{2-}\) + Cl\(^-\) → Cl\(^\bullet\) + SO\(_4^{2-}\)).\(^{71,72}\) As a result, even though Cl\(^-\) reacts more rapidly with *OH than SO\(_4^{2-}\) (*k*(Cl\(^-\)) = 4.3 × 10\(^8\) M\(^-1\)s\(^{-1}\) for *OH\(^{73}\) and *k* = 3.1 × 10\(^8\) M\(^-1\)s\(^{-1}\) for SO\(_4^{2-}\)^{74})\), Cl\(^-\) causes a more severe retarding effect on pollutant degradation kinetics, greater production of reactive chlorine species, or a switch of the main oxidant (from SO\(_4^{2-}\) to *OH) in SO\(_4^{2-}\)-AOP than *OH-AOPs.\(^{75-78}\)

A complication arises when halide ions are present at high concentrations (e.g., brackish ground water, saline wastewater, and reverse osmosis concentrate). A suite of halide radicals including X\(^\bullet\), X\(_2^\bullet\), XY\(^\bullet\) (mixed-halogen radical such as BrCl\(^\bullet\)) and OX\(^\bullet\) form at considerable concentrations.\(^{79}\) X\(^\bullet\) reacts with H\(_2\)O/OH\(^-\) at low halide levels to yield HOX\(^\bullet\) as an intermediate, which readily transforms into *OH under non-acidic conditions.\(^{78,79}\) Further reactions involving X\(^\bullet\) and X\(_2^\bullet\) lead to the formation of X\(_2\) (X\(^\bullet\) + X\(_2^\bullet\) → X\(_2^\bullet\) + X\(^-\); X\(_2^\bullet\) + X\(_2^\bullet\) → X\(_2^\bullet\) + 2X\(^-\)) and HOX (X\(_2^\bullet\) + H\(_2\)O → HOX + X\(^-\) + H\(^+\)).\(^{79}\) These reactive halogen species are more selective than SO\(_4^{2-}\) and *OH despite relatively high standard reduction potentials (E\(^0\)(Cl\(^\bullet\)/Cl\(^-\)) = 2.5 V\(_{\text{NHE}}\); E\(^0\)(Cl\(_2^\bullet\)/Cl\(^-\)) = 2.2 V\(_{\text{NHE}}\); E\(^0\)(Br\(^\bullet\)/Br\(^-\)) = 2.0 V\(_{\text{NHE}}\); E\(^0\)(Br\(_2^\bullet\)/Br\(^-\)) = 1.7 V\(_{\text{NHE}}\)).\(^{79}\) Consequently, the treatment efficiency tends to decrease, especially for the target compounds that are less reactive to reactive halogen species (e.g., benzoic acid).\(^{76}\) For the same reason, it is possible that the SO\(_4^{2-}\)-AOP becomes more efficient when target pollutants are more susceptible to oxidation by reactive chlorine species compared to SO\(_4^{2-}\) or *OH.\(^{80}\) This has caused some erroneous claims of the positive effects of Cl\(^-\) on persulfate-AOP,\(^{76,81}\) since HOCl, which has a much longer lifetime, can become the main oxidant in high Cl\(^-\) conditions, contrary to the intention of utilizing SO\(_4^{2-}\). Two-electron oxidation of halide ions by PMS (k(Cl\(^-\)) = 2.1 × 10\(^{-3}\) M\(^{-1}\)s\(^{-1}\); k(Br\(^-\)) = 7.0 × 10\(^{-1}\) M\(^{-1}\)s\(^{-1}\); k(\(\Gamma\)) = 1.4 × 10\(^3\) M\(^{-1}\)s\(^{-1}\))\(^{82}\) leads to direct HOX formation involving no halide-containing radicals as intermediates (Figures 3b and 3c), which creates binary mixtures of PMS and halide (e.g., PMS/Cl\(^-\), PMS/Br\(^-\), PMS/\(\Gamma\)) that can oxidize selected electron-rich organics.\(^{13,82-86}\) Note that mixtures of PMS and salts of Cl\(^-\) and Br\(^-\) are used for the synthesis of chlorinated and brominated olefins.\(^{87}\)

A major challenge in treating water containing halide ions and background NOM/EfOM (or target organics) by the persulfate-AOP comes from the formation of toxic halogenated byproducts such as trihalomethanes (THMs) and haloacetic acids (HAAs) (or halogenated intermediates) through the halogenation of NOM by HOX.\(^{13,85,88-91}\) Since the reactivity of PMS toward halide increases in the order of Cl\(^-\) < Br\(^-\) < \(\Gamma\),\(^{82}\) brominated and iodinated byproducts can be formed in addition to chlorinated byproducts. They are typically more toxic than the chlorinated analogues by a factor of >10 and >100, respectively.\(^{92,93}\) Whereas SO\(_4^{2-}\) dehalogenates halogenated organic byproducts
to release halide ions, some organics were found to become more susceptible to halogenation due to reaction with SO$_4^{2-}$ (e.g., conversion of carboxylic substituents on the aromatic rings to hydroxyl groups).

Unlike organic halogenation, the formation of toxic halogen-containing oxyanions such as ClO$^-_4$ and BrO$_3^-$ majorly involves SO$_4^{2-}$ attack, due to the inability of PMS to further oxidize HOX as a precursor to oxyanions (Figure 3b). Nevertheless, I$^-$ can be converted by PMS to IO$_3^-$ as a desired end product because of the easier oxidizability of HOI (Figure 3b). Br$^-$ is of more problematic than Cl$^-$ since (i) Br$^-$ is more reactive toward SO$_4^{2-}$ and PMS than Cl$^-$; (ii) HOBr• that forms from the reaction of Br• and OH•, unlike HOCl•, does not readily decay back to *OH and Br• ($k = 3.3 \times 10^7$ s$^{-1}$ for HOBr• decay; $96 k = 6.1 \times 10^9$ s$^{-1}$ for HOCl• decay); and (iii) bromination of phenols proceeds with second-order rate constants that are about three orders of magnitude higher than for chlorination. In addition, further oxidation of HOBr/OBr$^-$ by SO$_4^{2-}$ can lead to the formation of BrO$_3^-$. Note that BrO$_3^-$ formation is inhibited in the presence of dissolved organic matter mainly due to the formation of superoxide radical. It is also suppressed in traditional UV-based AOPs that employ H$_2$O$_2$, due to a reduction of HOBr to Br$^-_2$ by H$_2$O$_2$.

Interaction with OH•. Raising the pH above ca. 8.5-9 can cause a transition from SO$_4^{2-}$-dominated to *OH-dominated oxidation process. This results from an one-electron oxidation of OH• by SO$_4^{*}$ ($k = 6.5 \times 10^7$ M$^{-1}$s$^{-1}$) that is kinetically preferred over the reverse reaction (*OH + HSO$_4^-$ → SO$_4^{2-}$ + H$_2$O; $k = 6.9 \times 10^5$ M$^{-1}$s$^{-1}$). A change of the main oxidant from SO$_4^{2-}$ to *OH leads to a more effective abatement of organic compounds that persist in persulfate activation, but the enhancing effect can be offset by unwanted competitive reactions involving the less selective *OH. *OH is more significantly consumed than SO$_4^{2-}$ by natural water matrix components (e.g., NOM and CO$_3^{2-}$) and PMS/PDS. Regardless, increasing the pH has been employed as a simple approach for persulfate activation. The major oxidant in the activation process varies depending on whether PMS or PDS is used. Alkaline conditions initiate nucleophilic attack of PMS (SO$_5^{2-}$) to the peroxide oxygen of PMS (HSO$_5^-$), which results in the self-decay of PMS and the associated 1$^2$O$_2$ production (Figure 3c). In contrast, base activation of PDS occurs in two sequential reactions: (i) HO$_2^-$ formation through base-catalyzed PDS hydrolysis and (ii) reduction of PDS by HO$_2^-$ to SO$_4^{2-}$ (which further converts to *OH in highly alkaline conditions, e.g., at pH 12)

Interaction with Oxyanions. Anions such as phosphate (i.e., HPO$_4^{2-}$/H$_2$PO$_4^{2-}$) and bicarbonate/ carbonate (HCO$_3^-$/CO$_3^{2-}$) can scavenge SO$_4^{2-}$ ($k = \sim 10^6$ - $10^7$ M$^{-1}$s$^{-1}$) and decrease the overall efficiency of the SO$_4^{2-}$-AOPs. The radical scavenging becomes more noticeable when pH exceeds the $pK_a$ values of the corresponding acid of an anion. For instance, HPO$_4^{2-}$, the dominant species at pH $> pK_{a2} = 7.2$, exhibits two orders of magnitude greater reactivity toward SO$_4^{2-}$ than H$_2$PO$_4^-$: $k$(HPO$_4^{2-}$) = $1.2 \times 10^6$ M$^{-1}$s$^{-1}$ and $k$(H$_2$PO$_4^-$) < $7 \times 10^4$
In case of HCO$_3^−$/CO$_3^{2−}$, the second order rate constants for the reaction with SO$_4^{•−}$ are of the same order of magnitude but also higher for the deprotonated species: $k$(HCO$_3^−$) = $1.6 \times 10^6$ M$^{−1}$s$^{−1}$ and $k$(CO$_3^{2−}$) = $6.1 \times 10^6$ M$^{−1}$s$^{−1}$. However, a greater scavenging at a pH above the $pK_{a2}$ = 10.3 is also observed, since the main oxidant changes from SO$_4^{•−}$ to OH, which is more readily quenched by CO$_2^{2−}$, with $k$(HCO$_3^−$) = $8.5 \times 10^6$ M$^{−1}$s$^{−1}$ and $k$(CO$_3^{2−}$) = $3.9 \times 10^8$ M$^{−1}$s$^{−1}$, leading to the formation of CO$_3^{3−}$. NO$_2^−$ also rapidly reacts with SO$_4^{•−}$ ($k$ = $8.8 \times 10^8$ M$^{−1}$s$^{−1}$), thus significantly decelerating organic oxidation by activated persulfate, while NO$_3^−$ does not react with SO$_4^{•−}$. 

Formation of anion-derived radicals from the reaction between anions and SO$_4^{•−}$ brings another complication to the system. In addition to reducing the overall oxidation kinetics, these weaker oxidants (e.g., $E^0$(CO$_3^{•−}$/CO$_3^{2−}$) = 1.63 V)$^{108}$ are very selective and preferentially abate specific classes of electron-rich organics and lead to products that are not typically expected with SO$_4^{•−}$. In natural waters and wastewater effluents, CO$_3^{•−}$ often becomes the dominant oxidant due to HCO$_3^−$/CO$_3^{2−}$ oxidation not only by SO$_4^{•−}$ but also by aforementioned halogen radicals. $^{106}$ For example, Cl$^•$ and Cl$_2^{•−}$ formed through one-electron abstraction from Cl$^−$ by SO$_4^{•−}$ have relatively high second order rate constants for their reactions with HCO$_3^−$/CO$_3^{2−}$ ($k$ = $8 \times 10^7$ and $5 \times 10^8$ M$^{−1}$s$^{−1}$, respectively). $^{106}$ Since the rate constants for CO$_3^{•−}$-induced oxidation of organics range from as low as $4 \times 10^6$ to $1 \times 10^8$ M$^{−1}$s$^{−1}$ $^{35, 64, 112, 114}$ the treatment efficiency generally decreases. However, the kinetics of the oxidation of alkenes and activated aromatic compounds are less affected due to a relatively high susceptibility of electron-rich structure to the oxidation by CO$_3^{•−}$. For example, the kinetics of the oxidation of substituted anilines and phenoxides are barely affected, since CO$_3^{•−}$ reacts with them at diffusion-limited rates. $^{114}$ CO$_3^{•−}$ selectively oxidizes chemical moieties such as anilines, because they are oxidized primarily via electron abstraction by CO$_3^{•−}$, $^{106, 112, 113}$ leading to products such as nitro derivatives. $^{112}$

NO$_2^•$ formed from NO$_2^−$ due to one electron abstraction by SO$_4^{•−}$ is a mild oxidant ($E^0$(NO$_2^•$/NO$_2^−$) = 1.03 V$^{77}$) that can result in nitration of select organics such as (substituted) phenols. $^{110, 111}$ Note that aromatic nitrations also take place in conventional AOPs in a similar fashion. $^{115-117}$ but multiple nitrations yielding highly toxic polynitrophenols and nitrated biphenyls occurs only during the SO$_4^{•−}$-AOPs of water containing excess NO$_2^−$. $^{110, 111}$ The difference in the primary reaction pathway between OH and SO$_4^{•−}$ is noteworthy in this case. OH-adducts (i.e., hydroxycyclohexadienyl radical derivatives) rapidly react with oxygen and undergo further decay to ring-opening products. In contrast, phenoxy radicals formed via electron abstraction by SO$_4^{•−}$ is not prone to oxygenation but available for NO$_2^•$ attack and self-recombination. $^{110, 111}$ Formation of organic nitrogen compounds as undesired products highlights a need for pre-treatment prior to SO$_4^{•−}$-AOP of nitrite-rich waters.

It should also be noted that some anions such as HCO$_3^−$ and HPO$_4^{2−}$ can directly activate persulfate.
(mostly PMS) (Figure 3c).\textsuperscript{118-121} The peroxide bond of PMS is unsymmetrical, and it can easily undergo cleavage to form $\text{SO}_4^{\text{2-}}$ due to nucleophilic attack by these anions.\textsuperscript{119, 120} Alternatively, a transient complex can form from the nucleophilic attack by (poly)phosphates and produce $^{1}\text{O}_2$ during self-decay.\textsuperscript{121} Select anions can also be converted to peroxyanions due to oxygen atom transfer from PMS (e.g., $\text{HCO}_3^-$ from $\text{HCO}_2^-$ and $\text{HPO}_4^{2-}$ from $\text{HPO}_4^{2-}$) which are moderate oxidants ($E^0(\text{HCO}_4^-/\text{HCO}_3^-) = 1.8\text{ V}\textsuperscript{122, 118}$). Similar peroxyanion formation has been reported in direct oxidation of anions by $\text{H}_2\text{O}_2$.\textsuperscript{122-124} These oxyanions not only naturally occur but are widely used in laboratory studies at high concentrations as pH buffers, potentially complicating the interpretation of experimental results.

**CAN SINGLET OXYGEN BE A MAJOR OXIDANT?**

**Production Mechanism.** The findings that select persulfate-AOPs apparently degraded organic pollutants without involving $\text{SO}_4^{\text{2-}}$ and $\text{HO}^\text{•}$ initiated speculation on alternative non-radical mechanisms. Among them, singlet oxygenation has been proposed as the most likely pollutant oxidation pathway in some past studies.\textsuperscript{9, 11, 12, 125-128} It is indeed well known that $^{1}\text{O}_2$ forms via the self-decay of peroxy acids such as PMS, peracetic acid (PAA), and monoperphthalic acid at pH above their $pK_a$ values (\textasciitilde 8.2 - 9.3)\textsuperscript{66} following the reaction (in case of PMS): $\text{HSO}_5^- + \text{SO}_2^{2-} \rightarrow \text{HSO}_4^- + \text{SO}_4^{2-} + \text{O}_2$ (Figures 3c and 4). In alkaline conditions, ketone functionality in organics (e.g., $\text{p}$-benzoquinone, cyclohexanone) can also catalyze $^{1}\text{O}_2$ production through a cascade of reactions as follows: nucleophilic addition of PMS to ketone, formation of dioxirane as an intermediate, and reaction of dioxirane with PMS, which leads to ketone recovery and $^{1}\text{O}_2$ yield.\textsuperscript{11, 129} However, $^{1}\text{O}_2$ production through uncatalyzed PMS self-decay involving $\text{HSO}_5^-$ and $\text{SO}_2^{2-}$ is relatively inefficient ($k = 4.7 - 5.9 \times 10^{-2}\text{ M}^{-1}\text{s}^{-1}$ at pH = ca. 9 - 10)\textsuperscript{66} and is not likely a major mechanism for this AOP. For example, degradation of phenol is initially very slow when PMS is applied in alkaline condition due to a slow $^{1}\text{O}_2$ formation. Gradual acceleration of the kinetics is likely related to accumulation of quinone that enhances $^{1}\text{O}_2$ production from PMS self-decay.\textsuperscript{65}

In contrast, many recent studies suggest that $^{1}\text{O}_2$ can be produced \textit{en mass} to drive persulfate-AOPs even in acidic and neutral conditions. PMS and PDS self-decay is claimed to be catalyzed by carbonaceous materials such as surface-modified and heteroatom-doped carbon nanotubes (CNTs) and graphene\textsuperscript{125, 127, 130} as well as metal-derived nanomaterials such as $\text{Pd}/\text{g-C}_3\text{N}_4$ and $\text{LaMnO}_3$.\textsuperscript{12, 126, 131, 132} In case of PDS, an alternative mechanism involving PDS hydrolysis catalyzed by CNTs, $\beta$-MnO$_2$, $\text{Pd/C}_3\text{N}_4$, and Fe/montmorillonite has been proposed ($\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} \rightarrow \text{HO}_2^- + 2\text{SO}_4^{2-} + 3\text{H}^+$; $\text{S}_2\text{O}_8^{2-} + \text{HO}_2^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{H}^+ + \text{O}_2^\text{•}$),\textsuperscript{103} where the intermediate $\text{O}_2^\text{•}$ (or $\text{HO}_2^\text{•}$) is hypothesized to form $^{1}\text{O}_2$ through proton-promoted disproportionation ($\text{O}_2^\text{•}^- + \text{HO}_2^\text{•} \rightarrow ^{1}\text{O}_2 + \text{HO}_2^\text{•}$) (Figure 4).\textsuperscript{133} A line of evidence supporting the claim that $^{1}\text{O}_2$ plays a major role in this AOP includes: (i) oxidation of furfuryl alcohol (FFA) as a $^{1}\text{O}_2$ probe, (ii) endoperoxidation of anthracene derivative as a $^{1}\text{O}_2$ trap,\textsuperscript{11, 65} (iii) inhibitory impacts of L-histidine and azide as quenchers, (iv) EPR signals assigned to an $^{1}\text{O}_2$ adduct (or signals amplified in D$_2$O.
that extends the lifetime of $^1\text{O}_2$;\textsuperscript{12, 125-127, 130-132} and (v) quenching effects of benzoquinone for $\text{O}_2^\bullet$-intermediate.\textsuperscript{125, 128} Regardless of these observations, we find lack of plausible explanations on the role of catalysts in $^1\text{O}_2$ production via heterogeneous persulfate activation under non-alkaline condition.\textsuperscript{66, 103, 104} Carbonyl moieties which are required for accelerating PMS self-decay\textsuperscript{65, 129} are absent on the surface of most activators used in PMS studies.

Reactivity of singlet oxygen. $^1\text{O}_2$ is a highly selective oxidant that reacts almost exclusively with unsaturated organics via electrophilic addition and electron abstraction.\textsuperscript{134-137} In case of alkene, oxidation products with 1,2-, 1,3-, and 1,4-addition are observed depending on the structure.\textsuperscript{134, 135} The 1,2-cycloaddition occurs with electron-rich or sterically hindered olefins and the 1,3-addition (i.e., ene reaction) with allylic hydrogens, producing dioxetanes and allylic hydroperoxides, respectively. These unstable intermediates readily undergo bond cleavage or rearrangement to alcoholic or carbonyl fragments. The 1,4-addition (analogue to Diels-Alder reaction) and subsequent endoperoxide formation are frequently observed with conjugated dienes such as polycyclic aromatic or (hetero)aromatic hydrocarbons. Phenolic compounds with electron-donating substituents (e.g., alkyl and hydroxyl groups) can form radical cations (with intact benzene rings) or phenoxyl radicals via electron transfer to $^1\text{O}_2$ (forming $\text{O}_2^\bullet$).\textsuperscript{136-138} These radicals can undergo further oxygenation by ground-state oxygen or rearrangement to dioxetanes, yielding quinone-like and ring-opening products.\textsuperscript{136, 138} The selective nature of $^1\text{O}_2$ reaction has been exploited in fine chemical synthesis, such as controlled insertion of an oxygen moiety into organic substrates.\textsuperscript{139, 140}

The kinetics of $^1\text{O}_2$ reactions with most organic compounds are also much slower than for radicals and too slow to be practical in real world applications. For example, many phenolic compounds broadly used as target substrates exhibit too slow kinetics (their apparent second-order rate constants at pH = 7 ranging from $10^5$ to $10^6$ M$^{-1}$s$^{-1}$)\textsuperscript{141} for any meaningful degradation within a reasonable time scale (Table 1). In addition, the kinetics sensitively depend on the nature of substituents even for similar compounds; for example, the $^1\text{O}_2$ reactivity for substituted phenols varies by a factor of 100, from $k$ (4-nitrophenol) = $2.6 \times 10^5$ M$^{-1}$s$^{-1}$ to $k$ (4-chlorophenol) = $6.0 \times 10^6$ M$^{-1}$s$^{-1}$ and $k$ (4-hydroxyphenol) = $3.8 \times 10^7$ M$^{-1}$s$^{-1}$.\textsuperscript{141} The apparent second-order rate constants also strongly depend on pH. The deprotonated phenols (i.e., phenolate anions as the dominating species at pH > $pK_a$) are two or three orders of magnitude more susceptible to attack by $^1\text{O}_2$ than neutral phenols in most cases (i.e., $k = 10^6 - 10^9$ M$^{-1}$s$^{-1}$ for phenolates and $k < 10^5 - 10^6$ M$^{-1}$s$^{-1}$ for neutral phenols).\textsuperscript{137, 141}

The substrate-specific reactivity of $^1\text{O}_2$ and low oxidation potential of $^1\text{O}_2$ ($E^0(^1\text{O}_2/\text{O}_2^\bullet) = +0.81$ V$\textsuperscript{142}$) rather contradict to the purpose of AOPs, i.e., abating a wide range of organic compounds that are recalcitrant to other oxidants. A substrate-specific, selective reactivity, however, can be useful in some water treatment scenarios. For example, photosensitized water disinfection benefits from minimal interference of background organic matter and selectivity of $^1\text{O}_2$ toward oxidation of biomolecules (such as purine and pyrimidine bases in DNA/RNA, amino acids containing...
aromatic or sulfur functionalities in select proteins, and unsaturated fatty acids and steroids in lipid membranes.143, 144 This also explains the extensive use of $^{1}$O$_2$ in medical applications (e.g., selective oxidation of proteins in tumor cells) which involve an even more complex matrix.145

**Debatable Role of $^{1}$O$_2$.** From the kinetic data presented in Table 1, we find that the selective nature of $^{1}$O$_2$ often conflicts with the observations made in persulfate-AOPs that is claimed to involve $^{1}$O$_2$ as the main oxidant. For example, the decay of organics that are relatively inert toward $^{1}$O$_2$ (e.g., $k$(sulfamethoxazole) = (2 ± 1) × 10$^4$ M$^{-1}$s$^{-1}$, $k$(ofloxacin) = (5.6 ± 1) × 10$^6$ M$^{-1}$s$^{-1}$) has been presented as the evidence for the important role of $^{1}$O$_2$ in the persulfate-AOP.11, 65, 131, 132, 148

As another example, some studies reported effective decomposition of phenolic compounds in acidic and neutral pH regions (below their $pK_a$ values; $pK_a$(4-chlorophenol) = 9.41; $pK_a$(2,4-dichlorophenol) = 7.8).126, 127, 149 Other studies reported that the abatement of phenolic compounds was even retarded under alkaline conditions150 or was independent of the types of substrates.127, 149, 151-153 These observations contradict the pH-dependence of the reaction between these compounds and $^{1}$O$_2$.154 Further, half-lives of singlet oxygenation of widely used model substrates (i.e., acetaminophen, bisphenol A, and sulfamethoxazole) range from 15-600 hours (Table 1), questioning the claims that $^{1}$O$_2$ is primarily responsible for a rapid degradation observed with these target compounds. We find that total organic carbon (TOC) removal has also been erroneously used as an indication for singlet oxygenation.125, 130 $^{1}$O$_2$ is not powerful enough and too substrate-dependent to mineralize dissolved organic material.134-137

Some of these studies excluded the role of SO$_4^{*-}$ as a main oxidant based on observations such as the lack of quenching effect by alcohol-based scavengers and failure to observe an EPR signal corresponding to SO$_4^{*-}$. A critical piece of evidence to assure the involvement of $^{1}$O$_2$ often came from the observation that the kinetics of the target pollutant degradation was significantly retarded by the addition of excess L-histidine or azide (N$_3^-$), a commonly used $^{1}$O$_2$ quencher.126, 127, 130, 152 The steady-state concentration of $^{1}$O$_2$ was estimated using a probe compound such as FFA.12, 130 These conclusions require a careful reevaluation since these quenchers and probe can directly consume PMS.10, 155 The occurrence of 2,2,6,6-tetramethyl-1-piperidinylxoy (TEMPO) in the EPR spectra could be an inconclusive evidence of $^{1}$O$_2$ formation since 2,2,6,6-tetramethylpiperidine (TEMP) used as a spin trap forms in two routes: (i) direct oxidation of TEMP by $^{1}$O$_2$ and (ii) one-electron abstraction from TEMP as a heterocyclic amine156 followed by the combination of TEMP radical cation with O$_2$.157 In this regard, future studies should take advantage of a solvent-dependent lifetime of $^{1}$O$_2$ due to a solvent-specific capacity for physical quenching of $^{1}$O$_2$ ($k_d$(H$_2$O) = 2.5 × 10$^5$ s$^{-1}$; $k_d$(D$_2$O) = 1.5 × 10$^4$ s$^{-1}$; $k_d$(methanol) = 1.1 × 10$^5$ s$^{-1}$).154 Some reaction kinetics would increase up to three fold by the use of D$_2$O when $^{1}$O$_2$ is the major oxidant, which is unique compared to other transient species such as *OH and SO$_4^{*-}$.154

**ALTERNATIVE PERSULFATE ACTIVATION MECHANISMS**
Mediated Electron Transfer Mechanism. Compared to conventional AOPs that exclusively rely on •OH, persulfate-AOPs involve much more complex oxidation pathways, which alter depending on the water constituents and types of activators used. Table 2 underscores how sensitive the degradation pathways in persulfate-AOPs are to the choice of activator. Most notably, lines of evidence suggest that some oxidation pathways do not involve transient radical species such as SO$_4^{•−}$ or $^1$O$_2$ when persulfate is activated by carbon-based materials (e.g., CNTs, N-doped GO, annealed ND) and nanoscale metals/metal oxides (e.g., CuO, γ-MnO$_2$, Rh, Pt, Au). In addition to the aforementioned observations that rule out the contribution of SO$_4^{•−}$, there are a few unique behaviors that suggest an alternative non-radical pathway: (i) no occurrence of halogen-containing products (e.g., chlorinated phenols, BrO$_3^{−}$) at excess halides which should be expected if SO$_4^{•−}$ were present; (ii) the stability of persulfate with the above catalyst in the absence of organics (or alternatively, decay of persulfate only in the presence of electron-donating organics); (iii) degradation of organics by both PMS and PDS (e.g., transition metals such as Co and Mo selectively activate PMS); and (iv) emergence of electric current through activator (immobilized onto the electrode) only in the co-presence of organics and persulfate; and (v) difference in major intermediates that are different from those observed in SO$_4^{•−}$-AOPs or those expected by $^1$O$_2$ reaction.

One plausible mechanism in the above cases is direct electron transfer from organics (electron donor) to persulfate (electron acceptor) involving these conductive catalysts as electron transfer mediator (Figure 4). Instead of serving as a one-electron oxidant to form SO$_4^{•−}$ (e.g., M$^{n+}$ + HSO$_5^{−}$ → M$^{(n+1)+}$ + SO$_4^{•−}$ + OH$^{−}$), persulfate abstracts two electrons from organic compounds. Since persulfate is consumed only by organics, the persulfate consumption is reduced compared to other persulfate activation methods that continue to decompose persulfate, irrespective of whether or not organic pollutants exist. A formation of a reactive persulfate complex on the surface of highly conductive catalysts for electron transfer is likely involved. Accordingly, nitrogen doping of CNTs or a graphitic carbon shell formed during thermal annealing of ND are found to enhance the kinetics of this oxidation scheme due to enhanced surface interaction with the anionic PMS. Similar pathways seem to occur when other oxyanions such as periodate and PAA are used along with CNT.

High-valent metal formation. When metals ions such as iron(II), silver(I), and cobalt(II) are present in their reduced form, additional oxidation pathways can emerge (Figure 4). For example, two-electron oxidation of Fe(III) (complexed with an organic ligand or incorporated into the carbon matrix) by PMS leads to the formation of high valent iron-oxo species (i.e., $\equiv$Fe(V)=O, $\equiv$Fe(VI)=O). Similar to non-radical Fenton chemistry, organics can be oxidized by ferryl iron (i.e., Fe(IV)O$^{2+}$) as the transient reactive intermediate in the binary mixture of Fe(II) and PDS even under neutral conditions. If Fe(M)-driven oxidation (M = IV, V, and VI)
becomes a dominant reaction pathway, production of sulfone from sulfoxide via oxygen-atom transfer, which is unique to high valent iron, is likely to be observed.\textsuperscript{165} In addition, the reaction is not quenched by scavengers such as ethanol and other background organic matter.\textsuperscript{166} Similarly, PDS oxidatively transformed Ag(I) into high-valent silver, Ag(II), with a relatively high oxidizing capacity ($E^\circ(\text{Ag}^{2+}/\text{Ag}^+) = +1.98 \, \text{V}_{\text{NHE}}$).\textsuperscript{5} It is worth noting that Ag(II) is used to selectively oxidize aromatics and olefins in select organic syntheses.\textsuperscript{164} Finally, Co(III) can form when Co(II) is oxidized by PMS. Due to its high oxidation power ($E^\circ(\text{Co(III)}/\text{Co(II)} = +1.81 \, \text{V}_{\text{NHE}}$), Co(II) can become more efficient than SO$_4^{2-}$ in oxidizing Cl$^-$ and Br$^-$ into HOCl and HOBr. Although, it is not capable of further transforming HOCl (or HOBr) to ClO$_3^-$ (or BrO$_3^-$), formation of HOCl (or HOBr) as a secondary oxidant complicates the overall oxidation pathways.\textsuperscript{90, 95} The Co(II) phthalocyanine complex can produce high valent cobalt-oxo intermediates (i.e., Co(IV)) upon exposure to peroxides such as H$_2$O$_2$ and PMS (in the presence of HCO$_3^-$), initiating a non-radical oxidation of organics.\textsuperscript{170, 171}

**Direct oxidation.** PMS and PDS can oxidize alcohols, ketones, phenols, amines, and sulfides without involving radicals.\textsuperscript{38, 87, 172, 173} *Elbs oxidation* and *Boyland-Sims oxidation*, causing the hydroxylation of phenols and aryl amines, respectively, are primary mechanisms, though specific to PDS in most cases.\textsuperscript{174} Insertion of a hydroxyl moiety to aromatics proceeds via two sequential steps: (i) attack of phenolate anions (i.e., tautomeric carbanions) or unprotonated aryl amines on the peroxide oxygen of PDS followed by aryl sulfate formation and (ii) hydrolysis to yield hydroxyl aromatics that accompanies the S-O bond cleavage and resultant SO$_4^{2-}$ release.\textsuperscript{38, 175} This clearly differs from SO$_4^{2-}$-induced hydroxylation, since the kinetics was not retarded by allyl acetate as a radical trap and the hydroxylation efficiency was highly sensitive to the type of substituent.\textsuperscript{38} However, the role of PDS as a two-electron oxidant would be marginal in non-radical persulfate activation. Table 3 shows the half-lives of select aromatic compounds determined from second order rate constants for *Elbs* and *Boyland-Sims* persulfate oxidation. These half-lives do not match with the common time scales of the persulfate activation processes. Elevating the pH above the $pK_a$ values of aromatic substances favors PDS-mediated hydroxylation.\textsuperscript{38} Since the $pK_a$ values of many phenols are > 7 (unlike aryl amines), significant decay of substituted phenol by the persulfate-AOP under acidic and neutral conditions cannot be attributed primarily to direct PDS oxidation. Non-activated PMS also oxidizes select inorganic and organic substances, including As(III), $p$-aminobenzoic acid, sulfonamides, $\beta$-lactam antibiotics, and FFA.\textsuperscript{10, 176-179}

**PMS AND PDS ARE DIFFERENT**

Both PMS and PDS lead to SO$_4^{2-}$ generation and involve most of the chemistry discussed above, but they exhibit distinctively different properties (Table 4). Therefore, making a generalized claim on persulfate-AOP based on the observations made with one of them can be misleading. The differences between PMS and PDS in their reactivities mostly stem from the fact that the peroxide bond in PMS is asymmetrical with a partial positive charge induced on the peroxide oxygen.
attached to the hydrogen, while the peroxide bond in PDS is symmetrical in charge distribution.\textsuperscript{82, 86, 180} Therefore, the nonpolar PMS is more prone to nucleophilic attack by various nucleophiles (typically followed by oxygen atom transfer: \text{HSO}_5^- + A \rightarrow \text{HSO}_4^- + AO)^{82} including \(X^-, \text{CN}^-, \text{N}_3^-, \) and \(\text{HCO}_3^-\).\textsuperscript{10, 82, 180-182} Reaction of PMS with halide ions is of particular concern, since it implies that HOX can form even without involving persulfate activation (i.e., \text{SO}_4^{4-} formation).\textsuperscript{13, 82-86} PMS is rapidly depleted in excess of \(\text{N}_3^-\) prior to activation.\textsuperscript{10, 155} This reaction is not observed with PDS. Therefore, care must be taken when interpreting literature claims about the effects of halides (radical scavenger versus HOX precursor) and \(\text{N}_3^- (^{1}\text{O}_2\) quencher versus PMS scavenger) on the persulfate-AOP.

While PDS is rather inert to the reaction with \(X^-\) and \(\text{N}_3^-\), it can transform into \(\text{SO}_4^{4-}\) by a one-electron transfer upon the exposure to mild reducing agents such as \(\text{HO}_2^-\) and the semiquinone radical,\textsuperscript{67, 103} due to the relatively low dissociation energy of the peroxide bond (92 kJ•mol\(^{-1}\) for PDS and 377 kJ•mol\(^{-1}\) for PMS).\textsuperscript{183} This reaction is the base or a quinone-induced activation route producing \(\text{SO}_4^{4-}\), since \(\text{HO}_2^-\) and the semiquinone radical form as intermediates through alkaline hydrolysis of PDS and comproportionation reactions involving quinones, respectively.\textsuperscript{67, 103} It is worth noting that \(\text{HO}_2^-\) and the phenoxy anion activate PDS via reduction,\textsuperscript{68, 103} though they are good nucleophiles.\textsuperscript{184, 185} In contrast, PMS activation by base or quinone results from the nucleophilic addition of \(\text{SO}_3^{2-}\) to the peroxide oxygen of \(\text{HSO}_5^-\).\textsuperscript{11, 66, 104, 129} In addition, steric hindrance due to the presence of two \(\text{SO}_3\) moieties on both sides of a peroxide linker also makes PDS less reactive toward select organics as compared to PMS. For example, PMS more rapidly reacts with aromatic and aliphatic aldehydes\textsuperscript{186, 187} despite the higher redox potential of PDS than PMS (\(E^0(\text{HSO}_5^-/\text{HSO}_4^-) = +1.82\ \text{V}_{\text{NHE}}; E^0(\text{S}_2\text{O}_8^{2-}/\text{HSO}_4^-) = +2.08\ \text{V}_{\text{NHE}}\)).

The aforementioned structural differences between PMS and PDS lead to differences in specific activation processes. For instance, PMS is more effectively activated to yield \(\text{SO}_4^{4-}\) by transition metals (e.g., \text{Co(II)}, \text{CuFe}_2\text{O}_4, \text{Fe}_2\text{O}_3) than PDS due to the unsymmetrical molecular structure.\textsuperscript{17, 190, 191} PMS is also more efficient than PDS in oxidizing organics by carbonaceous materials and noble metal catalysts through the mediated electron transfer mechanism.\textsuperscript{7, 159, 162, 163} In contrast, energy transfer processes (i.e., photolysis, thermolysis) that homolytically break the peroxide bond more effectively activate PDS than PMS,\textsuperscript{20, 23, 119, 192} due to the lower bond dissociation energy. For example, PDS outperforms PMS in the quantum yield for radical production, with \(\Phi(\text{SO}_4^{4-}) = 1.4\) for PDS\textsuperscript{193} and \(\Phi(\text{SO}_4^{4-}) = 0.12\)\textsuperscript{194} and \(\Phi(\text{SO}_4^{4-} + \text{OH}) = 1.04\)\textsuperscript{195} for PMS under photolysis at ca. 250 nm. However, the relative treatment efficiency varies depending on the water matrix. The presence of background constituents such as \(\text{Cl}^-\) and \(\text{HCO}_3^-\) makes PMS superior to PDS in some cases. The reactions of PMS with natural nucleophiles improve \(\text{SO}_4^{4-}\) formation yields and produce secondary non-radical oxidants (e.g., \text{HOCl}), whereas inorganic impurities serve as radical scavengers in PDS processes.\textsuperscript{196, 197} Elevating the pH above the \(pK_a\) of PMS (i.e., 9.3)\textsuperscript{66} causes a tenfold increase in the molar absorption coefficient (from 13.8 to 149.5 M\(^{-1}\)cm\(^{-1}\)), thus
promoting radical production efficacy of the UV/PMS process. This is in contrast to UV/PDS in which the dominating species is switched from SO$_4^{*−}$ to *OH under alkaline conditions without changes in molar absorptivity and the associated radical formation yield. Note that PDS does not undergo protonation over a wide pH range due to the extremely low $pK_a$ value. Another distinction comes from the broad use of a triplet salt compound comprising KHSO$_5$, KHSO$_4$, and K$_2$SO$_4$ at molar ratios of 2:1:1 for PMS (called Oxone) in contrast to single potassium salt (K$_2$S$_2$O$_8$) for PDS.$^{87, 199}$ This mixed PMS salt contains less oxidants per mass, adds more sulfate species, and drops pH more drastically than PDS salts.$^{199}$

**MOVING FORWARD**

As persulfate-AOPs are rapidly progressing toward a mature subject of research with full-scale applications appearing in some sectors of water treatment,$^{200-202}$ it becomes more important to clearly understand the chemistry behind these processes. This is even more so, because they carry the term “advanced” oxidation that is commonly defined as a broadband treatment step to nonselectively abate a wide range of organic pollutants that cannot be readily treated by conventional oxidation processes. This connotation is not true in the case of the persulfate-AOPs. In contrast to *OH, which is the main oxidant in conventional AOPs, the primary radical species pursued in these processes, SO$_4^{*−}$, exhibits significant substrate specificity. In addition, other weaker and more selective oxidants such as $^1$O$_2$, HOX, and high-valent metals (e.g., Fe(VI)) are also formed depending on the route of persulfate activation and the water matrix. Some persulfate-AOPs, especially when the persulfate activation involves heterogeneous catalysts, do not even involve radical species. This departure from the convention in fact provides an unconventional opportunity in search for niche application development. In contrast to traditional AOPs, persulfate-AOPs provide the opportunity to tailor to certain oxidants and oxidation mechanisms depending on the water matrix and persulfate activation methods.

Figure 5 compares the second order rate constants for the reactions of select oxidants, including *OH, SO$_4^{*−}$, $^1$O$_2$, and O$_3$ with different classes of organic compounds. Generally, SO$_4^{*−}$ lies between the strong, low-selective *OH and weaker, more selective non-radical oxidants. The same claim can be made by comparing $\rho$ values of the relative reactivity toward (low $\rho$ for low selectivity, high $\rho$ for high selectivity), for example, substituted benzene derivatives (obtained from Hammett correlations): $\rho = −0.5$ for *OH,$^{31}$ $\rho = −2.4$ for SO$_4^{*−}$,$^{31}$ $\rho = −3.1$ for O$_3$,$^{203}$ and $\rho = −8.0$ for Fe(VI).$^{204}$ In essence, SO$_4^{*−}$ typically exhibits one or two orders of magnitude smaller second order rate constants than *OH, but it outperforms non-radical oxidants such as O$_3$ and $^1$O$_2$ regardless of substrate type. By carefully choosing the target pollutants, persulfate-AOPs can be an appealing treatment option, since it minimizes the loss of oxidation power due to oxidant scavenging by background water constituents, which is a prevalent challenge in *OH-based AOPs. Further opportunities exist to exploit the unique chemistry of persulfate-AOPs to achieve unconventional treatment goals. For example, one-electron oxidation by SO$_4^{*−}$ can degrade some organics such as...
cyanuric acid\textsuperscript{205} and perfluorooctanoic acid that are inert to $\cdot$OH,\textsuperscript{206, 207} though it is not yet considered an economically feasible technical option.\textsuperscript{208} Nevertheless, typically waters contain multiple organic contaminants, which requires broadband treatment options.

We believe these opportunities are best pursued by carefully characterizing the options and limitations of persulfate-AOPs and by fully appreciating the much more complex nature of chemistry involved. Persulfate studies made to date have been biased toward developing new activation strategies, often involving overly complex materials, without careful consideration of their potential for real world application.\textsuperscript{209} We instead suggest the future research to focus more on (i) developing standards for comparative evaluation among persulfate-AOPs (or between persulfate-AOPs and traditional AOPs) based on oxidant formation yield and chemical/energy consumption and (ii) establishing field-proven operating procedures to mitigate the occurrence of undesirable byproduct and side reactions in real water matrices. At the same time, we urge the researchers in this field to scrutinize various claims that are questioned throughout this article, including those related to the role of various oxidants and activation mechanisms, to better guide further research and technology development.

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**References**


56. Mora, V. C.; Rosso, J. A.; Martire, D. O.; Gonzalez, M. C., Phenol depletion by thermally activated peroxydisulfate at 70°C. *Chemosphere* **2011**, **84**, (9), 1270-1275.


92. Richardson, S. D.; Fasano, F.; Ellington, J. J.; Crumley, F. G.; Buettner, K. M.; Evans, J. J.; Blount, B. C.; Silva, L. K.; Waite, T. J.; Luther, G. W.; McKague, A. B.; Miltner, R. J.;


Ji, Y. F.; Wang, L.; Jiang, M. D.; Lu, J. H.; Ferronato, C.; Chovelon, J. M., The role of


193-199.


25


191. Jaafarzadeh, N.; Ghanbari, F.; Ahmadi, M., Catalytic degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) by nano-Fe₂O₃ activated peroxymonosulfate: Influential factors and mechanism determination. Chemosphere 2017, 169, 568-576.


208. Lutze, H. V.; Brekenfeld, J.; Naumov, S.; von Sonntag, C.; Schmidt, T. C., Degradation


239. Yang, S. Y.; Li, L.; Xiao, T.; Zheng, D.; Zhang, Y. T., Role of surface chemistry in...


Li Z; Liu D; Zhao Y; Li S; Wei X; Meng F; Huang W; Z, L., Singlet oxygen dominated peroxymonosulfate activation by CuO-CeO$_2$ for organic pollutants degradation: Performance and mechanism. *Chemosphere* 2019, **233**, 549-558.


Table 1. Second order rate constants for the reactions of singlet oxygenation with phenolic and pharmaceutical compounds and estimates of their half-lives during the exposure to singlet oxygen.

<table>
<thead>
<tr>
<th>Compound</th>
<th>pK&lt;sub&gt;a&lt;/sub&gt;</th>
<th>Rate constant, ( k ) (M&lt;sup&gt;-1&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Half-life, ( t_{1/2} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Undissociated form</td>
<td>Dissociated form</td>
<td>pH = 7</td>
</tr>
<tr>
<td>Phenol</td>
<td>9.9</td>
<td>( 2.6 \times 10^6 )</td>
<td>( 1.7 \times 10^8 )</td>
<td>2.8 \times 10^6</td>
</tr>
<tr>
<td>4-Chlorophenol</td>
<td>9.41</td>
<td>( 6.0 \times 10^6 )</td>
<td>( 1.9 \times 10^8 )</td>
<td>6.7 \times 10^6</td>
</tr>
<tr>
<td>2,4-Dichlorophenol</td>
<td>7.8</td>
<td>( 7.0 \times 10^5 )</td>
<td>( 1.4 \times 10^8 )</td>
<td>2.0 \times 10^7</td>
</tr>
<tr>
<td>2,4,6-Trichlorophenol</td>
<td>6.23</td>
<td>( 1.7 \times 10^7 )</td>
<td>( 1.4 \times 10^8 )</td>
<td>1.2 \times 10^8</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>4.98</td>
<td>( 2.0 \times 10^5 )</td>
<td>( 2.0 \times 10^8 )</td>
<td>2.0 \times 10^8</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>9.5</td>
<td>( 3.35 \times 10^5 )</td>
<td>( 2.26 \times 10^8 )</td>
<td>3.41 \times 10^5</td>
</tr>
<tr>
<td>2-Hydroxybenzoic acid</td>
<td>3.0; 13.8</td>
<td>( 2.5 \times 10^5 )</td>
<td>( 2.5 \times 10^5 )</td>
<td>( 2.5 \times 10^5 )</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>9.6</td>
<td>( 3.0 \times 10^5 )</td>
<td>( 2.0 \times 10^8 )</td>
<td>8.0 \times 10^5</td>
</tr>
<tr>
<td>Ofloxacin</td>
<td>5.45</td>
<td>( 5.6 \times 10^6 )</td>
<td>( 5.6 \times 10^6 )</td>
<td>( 5.6 \times 10^6 )</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>1.6; 5.7</td>
<td>( 2.0 \times 10^4 )</td>
<td>( 2.0 \times 10^4 )</td>
<td>( 2.0 \times 10^4 )</td>
</tr>
<tr>
<td>Sulfisoxazole</td>
<td>1.5; 5.0</td>
<td>( 5.5 \times 10^7 )</td>
<td>( 5.5 \times 10^7 )</td>
<td>( 5.5 \times 10^7 )</td>
</tr>
</tbody>
</table>

\(<t_{1/2}>^aEstimates of the half-lives of target substances \((t_{1/2})\) during singlet oxygenation, assuming that the steady-state concentration of \(^1\text{O}_2\), \([\text{^1O}_2]_{ss}\) ranges from \(9.6 \times 10^{-12} \) (\(t_{1/2}\) (FFA) = 10 min\(^{130}\)) to \(4.8 \times 10^{-11}\) M (\(t_{1/2}\) (FFA) = 2 min\(^{155}\)) \([\text{^1O}_2]_{ss}\) is computed based on the \(t_{1/2}\) value of FFA: \(\ln(2)/(k \times t_{1/2})\)).
\(<b>^b\)Measured at pH = 10.
\(<c>^c\)Measured at pH = 7.5.
\(<d>^d\)Measured in D<sub>2</sub>O at pD = 7.5.
\(<e>^eTotal quenching rate constant determined based on \(^1\text{O}_2\) consumption due to physical quenching and chemical reaction.
\(<f>^f\)Measured at pH = 10.2.
Table 2. Mechanisms for persulfate activation by homogeneous and heterogeneous catalysts. Note that the same materials have been reported to be involved in different activation mechanisms. We postulate the following reasons: (1) composite materials can initiate more than one activation mechanism; (2) the characteristics of materials are different even though they have the same nomenclature; (3) the same material can activate PMS versus PDS by different mechanisms; and (4) uncertainties in the mechanisms presented in some of the previous studies.

<table>
<thead>
<tr>
<th>Main oxidation mechanism</th>
<th>Activators</th>
<th>Materials</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radical-induced oxidation</td>
<td>Metal-based activators</td>
<td>Metal ions</td>
<td>Co^{2+}, Mn^{2+}, Fe^{2+}, Ce^{3+}, Ru^{3+}, Ag^{+}</td>
</tr>
<tr>
<td>Zero-valent metals</td>
<td>Fe^{0}, Cu^{0}, Al^{0}</td>
<td>163, 212-214</td>
<td></td>
</tr>
<tr>
<td>Metal oxides</td>
<td>Co_{3}O_{4}, Mn_{2}O_{3}, MnO, MgO, Fe_{2}O_{3}, CuFe_{2}O_{4}, ZnFe_{2}O_{4}, NiCo_{2}O_{4}, LaCoO_{3}, PrBaCo_{2}O_{5+δ}</td>
<td>215-224</td>
<td></td>
</tr>
<tr>
<td>Metal phosphides</td>
<td>CoP, Cu_{3}P</td>
<td>225, 226</td>
<td></td>
</tr>
<tr>
<td>Metal composites</td>
<td>Co/FeO_{2}, Co_{3}O_{4}/γ-FeOOH, MnO_{2}/ZnFe_{2}O_{4}, Fe/Ni, Co_{3}O_{4}/GO, Ni@N-doped CNT, Fe_{3}C@N-doped CNT, RuO_{2}/activated carbon</td>
<td>227-234</td>
<td></td>
</tr>
<tr>
<td>Carbon-based activators</td>
<td>N-doped CNT, N,S-codoped CNT, N(or P, B)-doped graphene, Mesoporous carbon, Activated carbon fiber, Annealed ND</td>
<td>8, 235-241</td>
<td></td>
</tr>
<tr>
<td>Singlet oxygenation</td>
<td>Metal-based activators</td>
<td>Metal oxides</td>
<td>MnO_{2}, biogenic MnO_{2}, CuO-CeO_{2}, LaMnO_{3}, LaNiO_{3}</td>
</tr>
<tr>
<td>Metal composites</td>
<td>Fe/montmorillonite, CoO-c-doped mesoporous carbon, CoFe_{2}O_{4}/graphite, Pd-g-C_{3}N_{4}, Fe_{3}C@N-doped CNT</td>
<td>126, 128, 229, 245, 246</td>
<td></td>
</tr>
<tr>
<td>Carbon-based activators</td>
<td>CNT, N-doped GO, N-doped graphene, Annealed ND, B-doped mesoporous carbon, Biochar</td>
<td>125, 127, 130, 148, 247-249</td>
<td></td>
</tr>
<tr>
<td>Mediated electron transfer</td>
<td>Metal-based activators</td>
<td>Metal oxides</td>
<td>CuO</td>
</tr>
<tr>
<td>Metal composites</td>
<td>Au/TiO_{2}, Pt/Al_{2}O_{3}, Rh/Al_{2}O_{3}</td>
<td>7, 24</td>
<td></td>
</tr>
<tr>
<td>Carbon-based activators</td>
<td>CNT, N-doped carbon nanosphere, Annealed ND</td>
<td>8, 9, 155, 160, 162, 163, 250</td>
<td></td>
</tr>
<tr>
<td>High valent metal-induced oxidation</td>
<td>Metal-based activators</td>
<td>Metal complexes and ions</td>
<td>Co(II)-phthalocyanine, Fe^{2+}, Ag^{+}</td>
</tr>
</tbody>
</table>
Table 3. Second order rate constants and half-lives for the Elbs and Boyland-Sims peroxydisulfate (PDS) direct oxidation\textsuperscript{a} of selected phenols and anilines.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate constant, $k$ (M$^{-1}$s$^{-1}$)\textsuperscript{b}</th>
<th>Half-life, $t_{1/2}$ (min)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>$1.9 \times 10^{-2}$</td>
<td>120-600</td>
</tr>
<tr>
<td>2-Nitrophenol</td>
<td>$1.5 \times 10^{-3}$</td>
<td>1500-7560</td>
</tr>
<tr>
<td>2-Methoxyphenol</td>
<td>$1.6 \times 10^{-2}$</td>
<td>144-720</td>
</tr>
<tr>
<td>2-Cresol</td>
<td>$8.4 \times 10^{-2}$</td>
<td>27.6-138</td>
</tr>
<tr>
<td>2-Methoxyphenol</td>
<td>$3.2 \times 10^{-1}$</td>
<td>7.2-36.6</td>
</tr>
<tr>
<td>Aniline</td>
<td>$1.2 \times 10^{-2}$</td>
<td>192-960</td>
</tr>
<tr>
<td>4-Nitroaniline</td>
<td>$3.0 \times 10^{-4}$</td>
<td>7680-38520</td>
</tr>
<tr>
<td>4-Chloroaniline</td>
<td>$1.5 \times 10^{-2}$</td>
<td>154.2-768</td>
</tr>
<tr>
<td>4-Methylaniline</td>
<td>$3.2 \times 10^{-2}$</td>
<td>72-360</td>
</tr>
<tr>
<td>4-Methoxyaniline</td>
<td>$1.7 \times 10^{-1}$</td>
<td>13.8-70.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Nucleophilic displacement on the peroxide oxygen of PDS takes place in the Elbs and Boyland-Sims oxidation reactions; phenolate anions and neutral aromatic amines serve as nucleophiles in the Elbs and Boyland-Sims oxidation, respectively. Rate constants for the oxidation of substituted phenols and anilines were measured under highly alkaline (i.e., 1.7 M KOH) and neutral (i.e., pH = 7) conditions, respectively.

\textsuperscript{b}Estimates of $t_{1/2}$ for a direct persulfate oxidation under first order conditions with PDS in large excess (1 mM) to the substrate ($t_{1/2} = \ln(2)/(k \times [PDS]_0)$).
Table 4. Comparison of physical-chemical properties, reactivities and main oxidants for PMS and PDS.

<table>
<thead>
<tr>
<th></th>
<th>Peroxymonomosulfate</th>
<th>Peroxydisulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard reduction potential ($E^0$)</td>
<td>1.82 $V_{\text{NHE}}$</td>
<td>2.08 $V_{\text{NHE}}$</td>
</tr>
<tr>
<td>Peroxide bond dissociation energy</td>
<td>377 kJ·mol$^{-1}$</td>
<td>92 kJ·mol$^{-1}$</td>
</tr>
<tr>
<td>Molar absorption coefficient at 248 nm</td>
<td>19.1 M$^{-1}$cm$^{-1}$</td>
<td>27.5 M$^{-1}$cm$^{-1}$</td>
</tr>
<tr>
<td>Acid dissociation constant ($pK_a$)</td>
<td>9.3$^{66}$</td>
<td>-3.5$^{251}$</td>
</tr>
<tr>
<td>Reactivity toward nucleophiles</td>
<td>Effective oxygen atom transfer reactions to nucleophiles such as $X^-$ and $\text{HCO}_3^-$ (leading to secondary oxidant formation)</td>
<td>Negligible (stable at excess background anions)</td>
</tr>
<tr>
<td>pH-dependent$^{41,77}$ pH $&lt; pK_a = 9.3$ ($\text{HSO}_5^-$) $k(\text{SO}_4^{2-}) &lt; 10^3$ M$^{-1}$s$^{-1}$ $k(\text{OH}) = 1.7 \times 10^7$ M$^{-1}$s$^{-1}$</td>
<td>$k(\text{SO}_4^{2-}) = 1.2 \times 10^6$ M$^{-1}$s$^{-1}$ $k(\text{OH}) &lt; 10^6$ M$^{-1}$s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>pH $&gt; pK_a = 9.3$ ($\text{SO}_4^{2-}$) $k(\text{SO}_4^{2-}) &lt; 10^3$ M$^{-1}$s$^{-1}$ $k(\text{OH}) = 2.1 \times 10^9$ M$^{-1}$s$^{-1}$</td>
<td>$k(\text{SO}_4^{2-}) = 1.2 \times 10^6$ M$^{-1}$s$^{-1}$ $k(\text{OH}) &lt; 10^6$ M$^{-1}$s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Main oxidant during activation by base and quinones</td>
<td>$^{1}\text{O}_2$ resulting from accelerated self-decay of PMS</td>
<td>$\text{SO}_4^{2-}$ resulting from PDS reduction</td>
</tr>
<tr>
<td>Preferred activation method</td>
<td>Electron transfer-based activation (e.g., catalysis with transition metals and nanocarbons)</td>
<td>Energy transfer-based activation (e.g., thermolysis, photolysis)</td>
</tr>
</tbody>
</table>
Figure 1. Activation of peroxymonosulfate (PMS) and peroxydisulfate (PDS) through electron and energy transferring processes.
Figure 2. Pathways for the oxidation of acetate and benzoate by hydroxyl radical and sulfate radical.
Figure 3. (a) Interaction of natural organic matter with peroxymonosulfate (PMS) and peroxydisulfate (PDS), (b) chemical transformation of halide ions by PMS and sulfate radical, and (c) generation of reactive intermediates through reaction of PMS with nucleophiles.
Figure 4. Possible oxidative reaction pathways induced by peroxymonosulfate (PMS) and peroxydisulfate (PDS) activation.
Figure 5. Comparison of selected oxidants (i.e., ozone, singlet oxygen, sulfate radical, and hydroxyl radical) in terms of their apparent second order rate constants ($M^{-1}s^{-1}$) for the reactions with organic and inorganic compounds.\textsuperscript{41, 77, 154, 203, 252, 253}
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