Can We Predict Intermediate-Radicals and Stable-Byproducts in Aqueous Phase Advanced Oxidation Processes using Computational Chemistry?

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Introduction to Advanced Oxidation Processes (AOPs)

- Why AOPs? How AOPs applied? Perspectives?
- What is needed to know?

- Challenges

- Findings using computational chemistry and experimental studies
Introduction - What are AOPs?

- Advanced Oxidation Processes (AOPs) that produce hydroxyl radicals (HO•-radicals) at ambient temperature and atmospheric pressure are attractive and promising water treatment technology.

- HO• radicals are highly reactive electrophiles, that react rapidly and non-selectively with the electron-rich sites of compounds.

- HO• radicals are capable of mineralizing organic compounds into carbon dioxide and water.

- AOPs may be used to control the emerging contaminants.

- Non-selectivity of HO• and radical chain reactions make AOPs complex processes as well as diversity and complexity of structure of a large number of emerging contaminants.
<table>
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<tr>
<th>Proved AOPs</th>
<th>Advantages</th>
<th>Disadvantages</th>
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| **H₂O₂/UV** | • Long stability and can be preserved prior to use of H₂O₂.  
• \( \text{H}_2\text{O}_2 + \text{UV} \rightarrow 2\text{HO}^\cdot + 3\text{O}_2 \) | • Poor UV absorption of H₂O₂  
• Interface of UV with the water matrix  
• Special reactors required for UV illumination  
• Residuals of H₂O₂ |
| **H₂O₂/O₃** | • Suitability for waters with poor UV light transmission  
• Special reactors requirement for UV illumination  
• \( \text{2O}_3 + \text{H}_2\text{O}_2 \rightarrow 2\text{HO}^\cdot + 3\text{O}_2 \) | • Stripped volatile organics  
• Expensive and inefficient to produce O₃  
• Residues of gaseous O₃  
• Difficulty of maintenance (O₃/H₂O₂ dosages)  
• Low pH is detrimental |
| **TiO₂/UV** | • Activated with near-UV light  
• Greater light transmission  
• \( \text{TiO}_2 + \text{UV} \rightarrow h^+ + e_{cb} \)  
• \( h^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HO}^\cdot \) | • Occurrence of fouling of catalyst  
• Recovery of TiO₂ required upon the use as a slurry |
Various AOPs Technologies 2/2

HiPOx ($O_3/H_2O_2$)

Applied Process Technologies, Inc

Purifics (UV/TiO$_2$)

0.5 MGD

Photo-Cat Purification

Low Pressure

UV system

($UV/H_2O_2$)
About 4% of the total electricity consumption in the US is for the water and wastewater sector (80% is for conveyance and distribution).

Wastewater treatment accounts for about 3% of the US electrical energy load.

The world’s largest Groundwater Replenishment System (GWRS) in Fountain Valley, CA, (54.5 MGD).

- RO 48%, MF 25%, Effluent pumping 18%, UV/H₂O₂ 7% and Misc 1%
- In GWRS, AOP uses approximately 0.08 kWh/m³ for 1.8–2.1 logs of removal (> 90-99 % removal) for NDMA and 1,4-Dioxane.

Secondary effluent from wastewater treatment

- Microfiltration
- Reverse Osmosis
- UV

Recharge into the wells
Treatment + collection (no distribution)
- 0.05 - 0.1 kWh/m³ (surface water treatment)
- 0.16 kWh/m³ (ground water treatment)
- 1.0-2.5 kWh/m³ (brackish groundwater)
- 2-4.5 kWh/m³ (seawater desalination)

- 0.25 kWh/m³ (trickling filter)
- 0.35-0.60 kWh/m³ (activated sludge)
- 0.40 kWh/m³ (advanced treatment without nitrification)
- 0.50 kWh/m³ (advanced treatment with nitrification)
AOPs Application for DOC removal of RO Retentate

Screen → Primary Clarification → Aeration → Secondary Clarification → Filtration → Disinfection

Microfiltration → Reverse Osmosis → Stabilization → Aquifer Storage and Recovery → Disinfection → Use

DOC: 40 ~ 50 mg/L
BDOC (biologically degradable DOC5): 4.5 mg/L
pH = 7.5-7.8

Westerhoff, Moon, Minakata, Crittenden, 2009, Water Research 43(16), 3992-3998
Energy consumption v.s. DOC % reduction among AOPs

- 5 kWh/lb $O_3$, 4.9 kWh/lb $H_2O_2$, 13.6 kWh/lb $TiO_2$
- Fenton's was excluded due to the limited DOC removal (49%)

![Graph showing DOC reduction and energy consumption for different AOPs.]

- HiPOx ($O_3/H_2O_2$)
- UV/$H_2O_2$
- UV/$TiO_2$
- Purifics ($UV/TiO_2$)
- UV/$TiO_2/H_2O_2$

**Initial DOC is diluted half from original RO retentate. ($DOC_0 \approx 20$ mg/L)**

**For all experiments, $TiO_2 = 2$ g/L and pH = 5.0**

Westerhoff, Moon, Minakata, Crittenden, 2009, Water Research 43(16), 3992-3998
Fate of Degradation Pathways of Organic Compounds in AOPs

\[ \text{hv} + \text{H}_2\text{O}_2 \]
\[ \text{O}_3 + \text{H}_2\text{O}_2 \]
\[ \text{hv} + \text{TiO}_2 \]
\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \]

\[ \text{HO}^• \]

\[ \text{DOM} \]

\[ \text{hv} \]

\[ \text{hv} \]

\[ \text{HO}^• \]

\[ \text{hv} \]

\[ \text{Cl}^• \]

\[ \text{NO}_3^- \]

\[ \text{Cl}^- \]

Alkalinity

\[ \text{O}_3 \]

\[ \text{O}_2 (\text{aq}) \]

\[ \text{RCOO}^• \]

\[ \text{RCOH} \]

\[ \text{RCOR}' \]

\[ \text{ROH} \]

\[ \text{CO}_2 \]

\[ \text{H}_2\text{O} \]

\[ \text{RCOOH} \]

Organic pollutant → Aldehydes → Carboxylic acids → Carbon dioxide and mineral acids
Proposed Reaction Mechanisms

Stefan and Bolton, 1998; 1999; 1999; Stefan et al., 1996; 2000; Cooper et al., 2009; Li et al., 2004; 2007; von Sonntag and Schuchmann, 1984; Schuchmann and von Sonntag, 1979 and references are therein.
Comparison of gaseous and aqueous $k_{\text{HO}}$.

- Significant mechanistic differences between the gaseous and aqueous phases (e.g., effect of hydrogen bond to the oxygenated compounds, cage effect, solvation, etc.)
\( k_{HO} \) with \( E(\text{HOMO-SOMO}) \)

- HOMO was calculated with AM1 for 477 compounds that includes alkanes, oxygenated, alkyl halides, alkenes, aromatic and S-, N- or P-atom-containing compounds.

\[ y = 0.499x + 13.503 \]
\[ R^2 = 0.512 \]

HOMO-SOMO (eV) vs. \( \log k_{HO} \) in the aqueous phase

\[ y = -0.671x + 5.536 \]
\[ R^2 = 0.599 \]

HOMO-SOMO (eV) vs. \( \log_{10}(k_{HO}) \) in the gaseous phase

SOMO (singly occupied molecular orbital) for HO\( \cdot \); -1.83 eV

Energy for stabilization
Group Contribution Method (GCM) for predicting $k_{\text{HO}^\cdot}$.

- Essence is same as the GCM for the gaseous phase developed by Dr. Roger Atkinson (EPA software AOPWIN).
- Experimental datasets compiles in Buxton et al., 1988 etc.

Hypothesis

- Observed experimental reaction rate constant for a given organic compound is the combined rate of all elementary reactions involving $\text{HO}^\cdot$, which can be estimated using Arrhenius kinetic expression.

- The $E_a$ consists of two parts based on Benson's thermochemical additivity concept (Benson, 1976):
  1. **Base part** from main reaction mechanisms (i.e., H-atom abstraction, HO· addition to alkenes and aromatic compounds and HO· interaction with S, N, or P-atom-containing compounds).
  2. **Functional group contribution** partially from neighboring and/or next nearest neighboring functional group.
Group Contribution Method and Update

Minakata, Li, Westerhoff, and Crittenden. ES&T 2009, 43, 6220-6227

- 257 rate constants (83% of 310 data) from calibration were within $0.5 \leq \frac{k_{\text{calc}}}{k_{\text{exp}}} \leq 2.0$.
- The sample deviation was 0.92. Degree of Freedom was 164
- 76 rate constants (62% of 124) from prediction were within $0.5 \leq \frac{k_{\text{calc}}}{k_{\text{exp}}} \leq 2.0$. 
"The wide application range in combination with the user-friendliness makes it probably the best currently available estimation tool for OH radical reactions in aqueous solution. Overall, the method of Minakata et al. is currently the most broadly usable method for the prediction of OH radical reaction rates in aqueous solution." Professor Hartmut Herrmann in ChemPhysChem, 2010, 11, 3796-3822.

Professor Urs von Gunten (Eawag, Swiss Federal Institute of Aquatic Science and Technology) referred to the GCM for HO radical rate constant predictions as "sophisticated estimation methods for HO radical rate constants" and used the GCM to calculate 29 HO radical reaction rate constants emerging organic contaminants and obtained an accuracy of difference of factor of 2 from experimental values (Wat. Res. 2012, 46, 6177-6195).

GCM provides Microsoft Excel spreadsheet and Compiled Fortran Program as Supplemental Materials in Minakata, Li, Westerhoff, Crittenden, 2009 ES&T 43, 6220-6227, so that any users can download and calculate the HO· rate constants for a compound of interest.
Challenges Remain

- Limitations for the GCM
  - Many datasets are required to calibrate parameters
  - Only deal with molecules for which all required group rate constants and group contribution factors have been calibrated before.
  - Limited number of literature-reported experimental rate constants for other reaction mechanisms than HO·
  - Assumed that a functional group has approximately the same interaction properties under a given molecule, so that the GCM disregards the changes of the functional properties that can arise from the intramolecular environment by electronic push-pull effects, hydrogen bond formation, or by steric effects.
According to a linear free energy relationship (LFER), for the same reaction mechanism, the difference in the free energy of activation of transition states I and R is proportional to the difference in free energy change of the reaction for species I and a reference species R to produce the products, C and D.

\[ \Delta E(\Delta E^*) \propto \Delta E(\Delta E_0) \]

\[ \ln k_I - \ln k_R = -\frac{E_{a,A*I}}{RT} + \frac{E_{a,A*R}}{RT} = -m'[E_{a,A*I} - E_{a,A*R}] \]

\[ \ln k_{Ri} - \ln k_{R0} = -\rho \left( \Delta G_{rxn,R_i}^{\neq} - \Delta G_{rxn,R_0}^{\neq} \right) = m \left( \ln \frac{K_{a,R_i}}{K_{a,R_0}} \right) \]
Linear Free Energy Relationships for \( \text{HO}\cdot \): \[ \ln k_{\text{exp}} = \rho \Delta G_{\text{aq, calc}} + \sigma \]

\text{Minakata and Crittenden, ES&T 2011, 45, 3479-3486}

\text{Minakata, Song, and Crittenden, ES&T, 2011, 45, 6057-6065}

\text{Minakata et al., 2011 in ACS Denver and 2013 in ACS New Orleans}
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