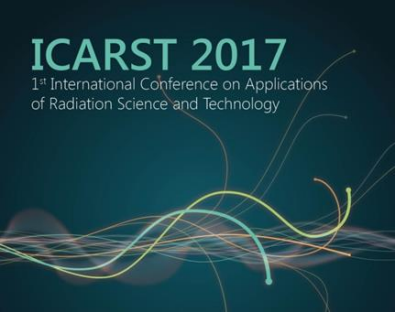


Basic radical reactions in water treatment by ionizing radiation

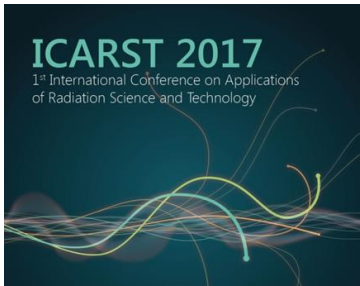
By: László Wojnárovits

Selectivity, rate constants, main reactions

Do up the buttons again
Gomboljuk újra a kabátot!

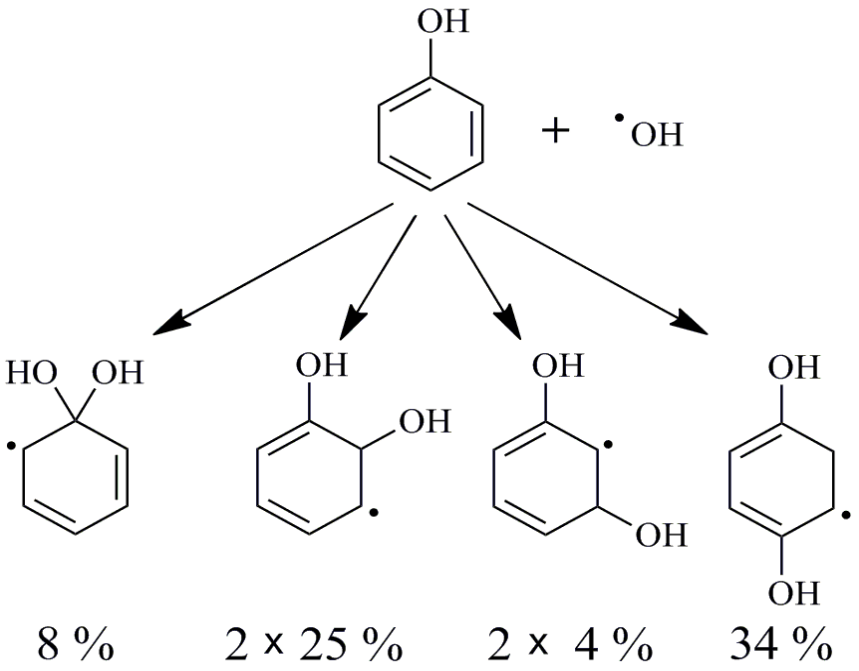
General believes:

1. $^{\bullet}OH$ is an unselective radical, it reacts with practically diffusion limited rate constant with most of organic molecules.
2. $^{\bullet}OH$ decomposes all organic pollutants.
3. The reductive intermediates, $e_{aq}^{\bullet-}$ and $H^{\bullet}$ induce reduction reactions
4. $^{\bullet}OH$ is the main reactive intermediate in most of AOP, including radiolysis.
5. In natural waters $^{\bullet}OH$ induces the degradation of harmful organic compounds



Hydroxyl radical (•OH), $E(^{\bullet}OH/OH^{-}) = 2.1$ V

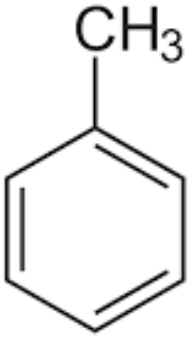
Selective radical, or non-selective radical

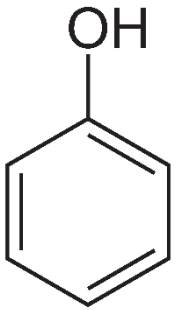


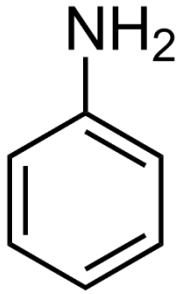
•OH addition to phenol.
Monitoring charge distribution

Selectivity in H-abstraction

Alcohol	Rate constant ($mol^{-1}\ dm^3\ s^{-1}$)	$-CH_3$ (%)	$-CH_2-$ (%)	-CH- (%)	-OH (%)
MeOH	9×10^8	93			7
EtOH	2.2×10^9	13.3	84.3		2.4
2-PrOH	2×10^9	13.3		85.5	1.2

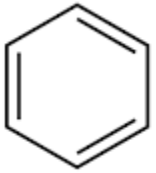






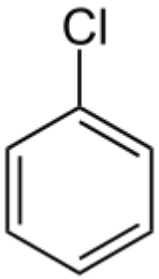
σ_p -0.17 -0.37 -0.66

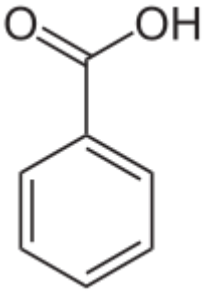
k_{OH} 8.1×10^9 8.4×10^9 8.6×10^9

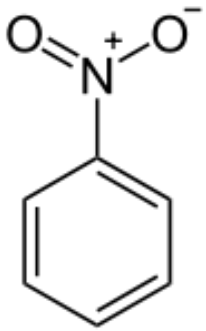


σ_p 0.0

k_{OH} 7.8×10^9

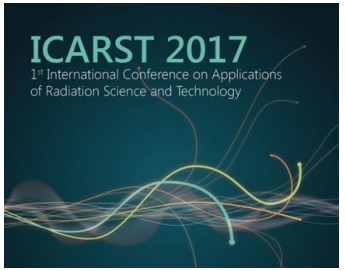






σ_p 0.23 0.45 0.78

k_{OH} 5.6×10^9 1.9×10^9 3.5×10^9

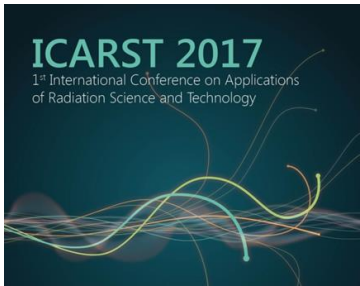


Whether the hydroxyl radical degrades all organic compounds, or not?

The rate constants of •OH reactions with several organic molecules are very low, e.g. with fluorine containing carboxylic acids, which are recalcitrant in •OH mediated degradation. For instance:

$$\bullet OH + CF_3COO^- \longrightarrow \text{products} \quad k < 10^6\ mol^{-1}\ dm^3\ s^{-1}$$

•OH does not degrade all organic molecules



Dichloride radical anion ($Cl_2^{\bullet -}$), $E(Cl_2^{\bullet -}/2\ Cl^-)$=2.1 V

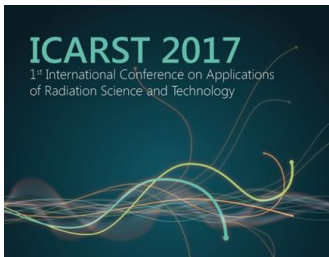
$$^{\bullet}OH + Cl^- \rightleftharpoons ClOH^{\bullet -} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} (HOClH)^{\bullet} \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} Cl^{\bullet} \underset{-Cl^-}{\overset{+Cl^-}{\rightleftharpoons}} Cl_2^{\bullet -}$$

Complexation is fast, in presence of Cl^- $Cl^{\bullet}$ does not react with the organic solutes. In the $^{\bullet}OH + Cl^-$ system below pH 5 $Cl_2^{\bullet -}$, above $^{\bullet}OH$ dominates

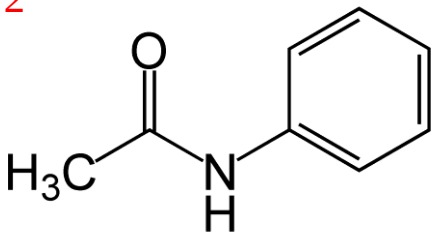
$Cl_2^{\bullet -}$ reacts in direct oxidation with aromatics with formation of an intermediate radical cation.

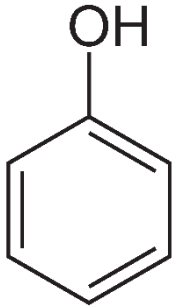
$$Cl_2^{\bullet -} + C_6H_5OH \xrightarrow{-2Cl^-} [C_6H_5OH]^{\bullet +} \longrightarrow H^+ + C_6H_5O^{\bullet}$$

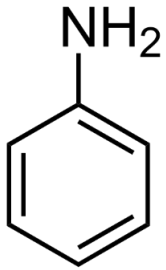
$$SO_4^{\bullet -} + Cl^- \rightleftharpoons SO_4^{2-} + Cl^{\bullet} \qquad k_f = 3.2 \times 10^8\ mol^{-1}\ dm^3\ s^{-1}$$
$$k_r = 2.5 \times 10^8\ mol^{-1}\ dm^3\ s^{-1}$$



$Cl_2^{\bullet-}$

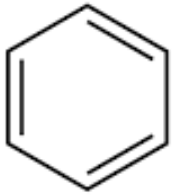






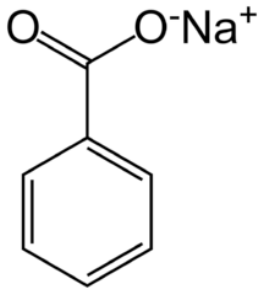
σ_p **0.0** **-0.37** **-0.66**

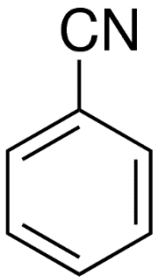
k_{OH} **2×10^7** **2.8×10^8** **1.2×10^7**



σ_p **0.0**

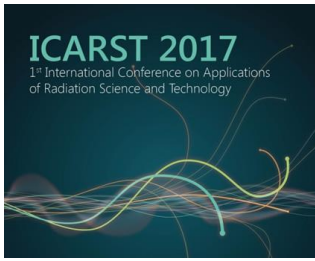
k_{OH} **2×10^5**





σ_p **0.0** **0.66**

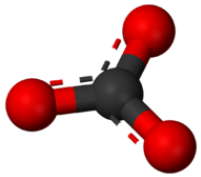
k_{OH} **2×10^4** **2×10^4**



Carbonate radical anion ($CO_3^{\bullet -}$), $E(CO_3^{-\bullet},H^+/HCO_3^-$, pH 7) = 1.78 V

$^{\bullet}OH + CO_3^{2-} \longrightarrow CO_3^{\bullet -} + OH^-$ $\quad k_3 = 3.9 \times 10^8\ mol^{-1}\ dm^3\ s^{-1}$

$^{\bullet}OH + HCO_3^- \longrightarrow CO_3^{\bullet -} + H_2O$ $\quad k_4 = 8.5 \times 10^6\ mol^{-1}\ dm^3\ s^{-1}$



The carbonate radical anion has a planar structure

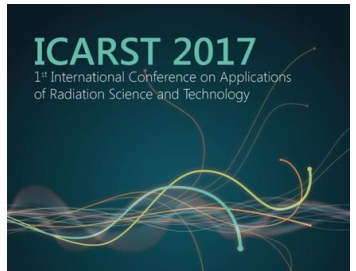
Carbonate radical anion reactions

$C_6H_5NH_2 + CO_3^{\bullet -} \longrightarrow CO_3^{2-} + [C_6H_5NH_2]^{\bullet +}$

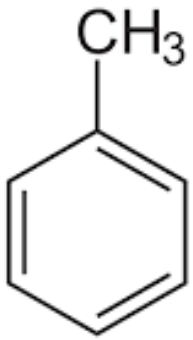
$k = 6.5 \times 10^8\ mol^{-1}\ dm^3\ s^{-1}$

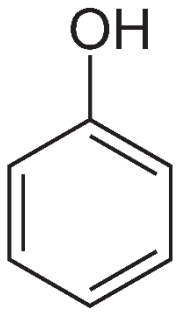
$C_6H_5O^- + CO_3^{\bullet -} \longrightarrow CO_3^{2-} + C_6H_5O^{\bullet}$

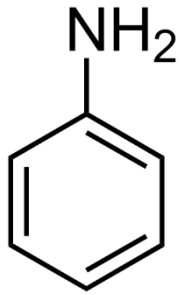
$k = 5 \times 10^7\ mol^{-1}\ dm^3\ s^{-1}$



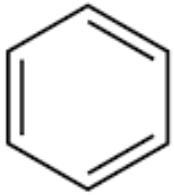
$CO_3^{\bullet-}$



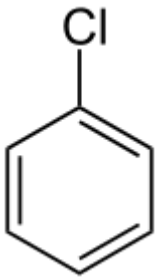


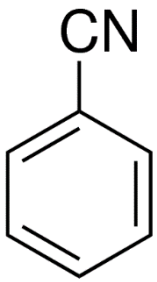


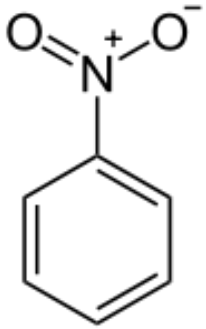
σ_p	-0.17	-0.37	-0.66
k_{OH}	5.6×10^4	5.9×10^6	6.5×10^8



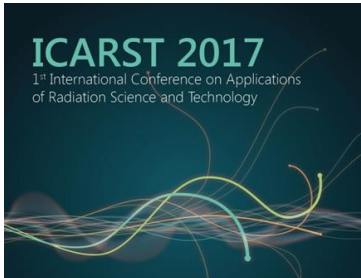
σ_p	0.0
k_{OH}	3×10^3 - 3.2×10^5







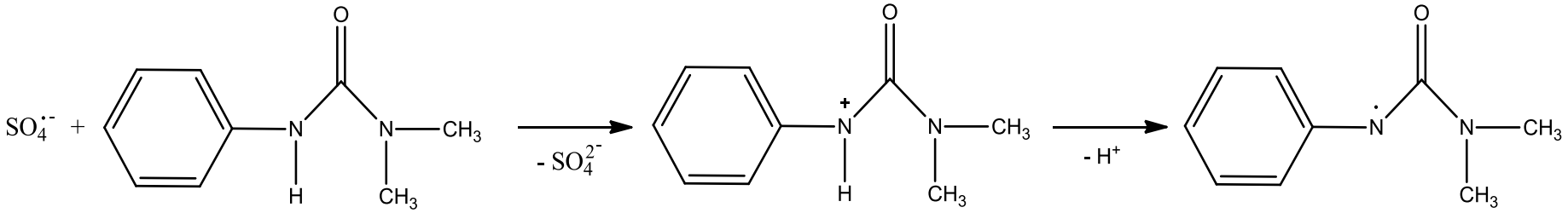
σ_p	0.23	0.66	0.78
k_{OH}	2.7×10^5	1.3×10^2	1.4×10^4

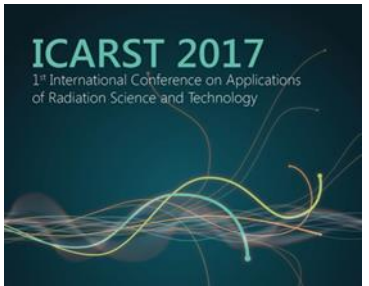


Sulfate radical anion. $E(SO_4^{\bullet -}/SO_4^{2-}) = 2.43\ V$

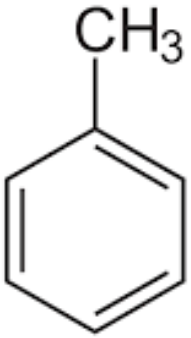
$$e_{aq}^{\bullet -} + S_2O_8^{2-} \longrightarrow SO_4^{\bullet -} + SO_4^{2-} \qquad k = 1.2 \times 10^{10}\ mol^{-1}\ dm^3\ s^{-1}$$

Strong electron acceptor, mainly reacts in electron transfer. Electron donating substituent increases, electron withdrawing substituent decreases the rate.



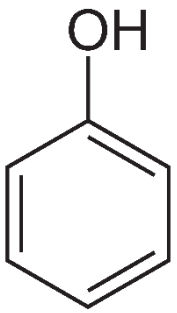


$SO_4^{\bullet-}$



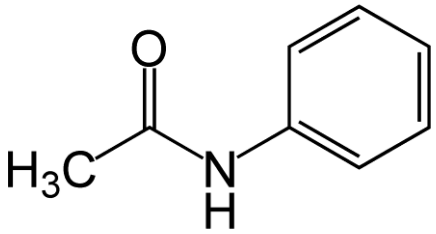
σ_p -0.17

k_{OH} 3.1×10^9



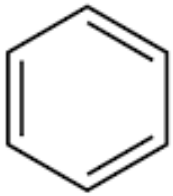
σ_p -0.37

k_{OH} 6.2×10^9



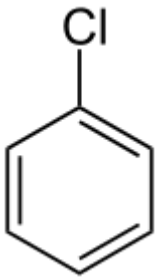
σ_p 0.0

k_{OH} 3.6×10^9



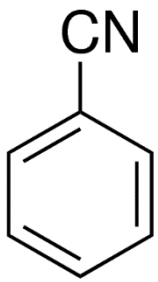
σ_p 0.0

k_{OH} 2.4×10^9



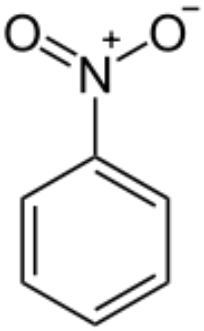
σ_p 0.23

k_{OH} 1.5×10^9



σ_p 0.66

k_{OH} 1.2×10^8



σ_p 0.78

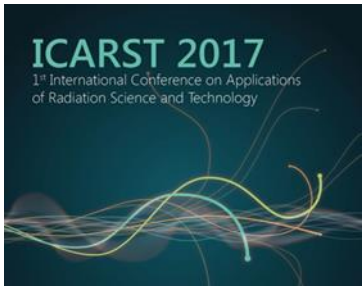
k_{OH} $\leq 10^6$

Hydrogen atom. $E(H_{aq}^{+}/H^{\bullet}) = -2.4$

$H^{\bullet}$, similarly to $^{\bullet}OH$, is also a pronounced electrophilic radical and thus shows a high regioselectivity in its addition reactions with unsaturated compounds, with saturated molecules H-atom abstraction occurs.

$$H^{\bullet} + C_6H_6 \longrightarrow {}^{\bullet}C_6H_7 \qquad 1.0 \times 10^9\ mol^{-1}\ dm^3\ s^{-1}$$

$$H^{\bullet} + CH_3OH \longrightarrow {}^{\bullet}CH_2OH + H_2 \qquad 2.6 \times 10^6\ mol^{-1}\ dm^3\ s^{-1}$$



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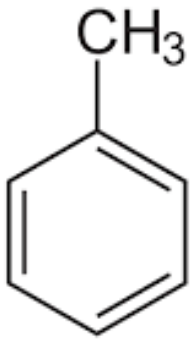
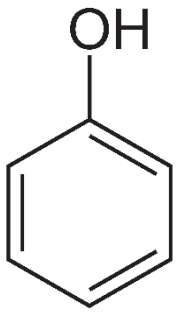
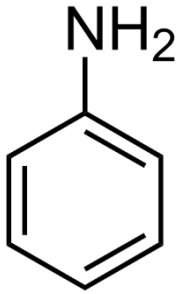
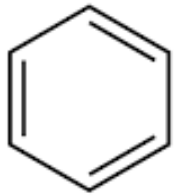






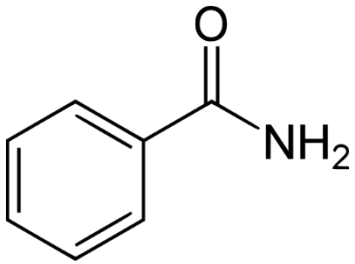
σ_p -0.17 -0.37 -0.66

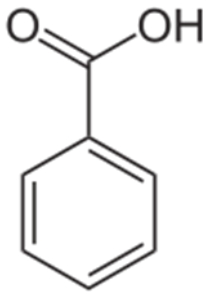
k_{OH} 2.6×10^9 2.0×10^9 2.2×10^9

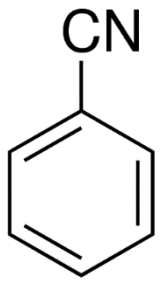


σ_p 0.0

k_{OH} 1×10^9

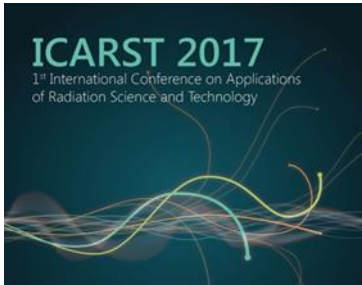






σ_p 0.36 0.45 0.66

k_{OH} 6.5×10^8 8.1×10^8 5×10^8



Hydrated electron. $E(\mathrm{aq}/e_{aq}^{\bullet -}) = -2.9$ V

The reaction with organic molecules mostly occurs by addition. However, the electron adduct often immediately protonates, in the protonation the same radical is produced as in $H^{\bullet}$ addition reactions.

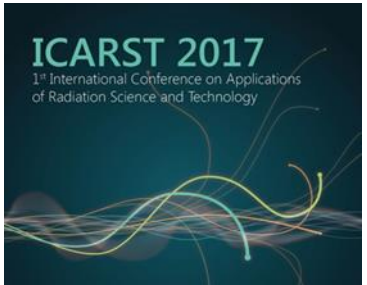
Reversible addition

$$e_{aq}^{\bullet -} + C_6H_6 \rightleftarrows C_6H_6^{\bullet -} \xrightarrow[-OH^-]{+H_2O} C_6H_7^{\bullet} \quad k = 1 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

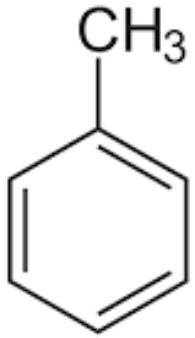
Dissociative electron capture

$$e_{aq}^{\bullet -} + C_6H_5Cl \longrightarrow [C_6H_5Cl^{\bullet -}] \longrightarrow C_6H_5^{\bullet} + Cl^- \quad k = 6.4 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

In $e_{aq}^{\bullet -}$ and $H^{\bullet}$ reactions with organic molecules mostly carbon centered radicals form, just like in $^{\bullet}OH$ reactions.

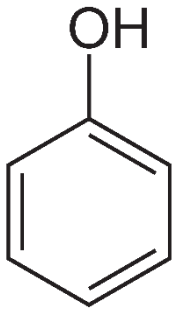


$e_{aq}^{\bullet -}$



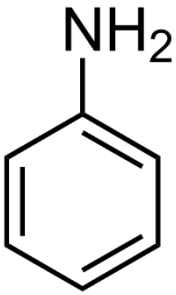
σ_p -0.17

k_{OH} 1×10^7



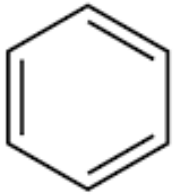
σ_p -0.37

k_{OH} 2×10^7



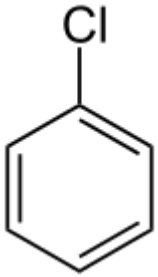
σ_p -0.66

k_{OH} 3×10^7



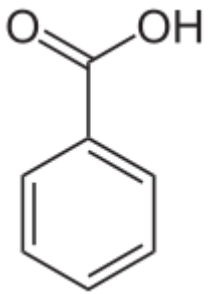
σ_p 0.0

k_{OH} 1×10^7



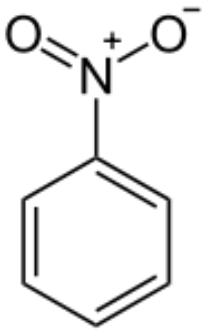
σ_p 0.23

k_{OH} 5×10^8



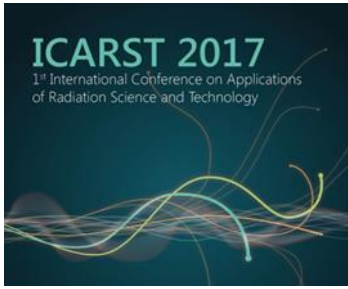
σ_p 0.45

k_{OH} 7.1×10^9



σ_p 0.78

k_{OH} 3.7×10^{10}



Rate constants of forward (k_f) and reversed (k_r) peroxyl radical forming/dissociation reactions of radicals and equilibrium constants (K).

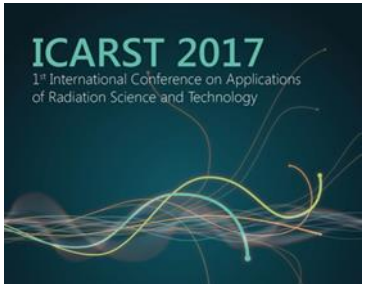
$$R^{\bullet} + O_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} ROO^{\bullet}$$

Radical	k_f , $mol^{-1}\ dm^3\ s^{-1}$	k_r , s^{-1}	K, $mol^{-1}\ dm^3$
Simple alkyl radicals			
c-$C_5H_9^{\bullet}$	3.5×10^9		
$^{\bullet}CH_2OH$	4.2×10^9		
Cyclohexadienyl radicals			
Anisol	8×10^8	3.9×10^4	2.1×10^4
Toluene	4.8×10^8	7.5×10^4	6.4×10^3
Benzene	3.1×10^8	1.2×10^4	2.6×10^4

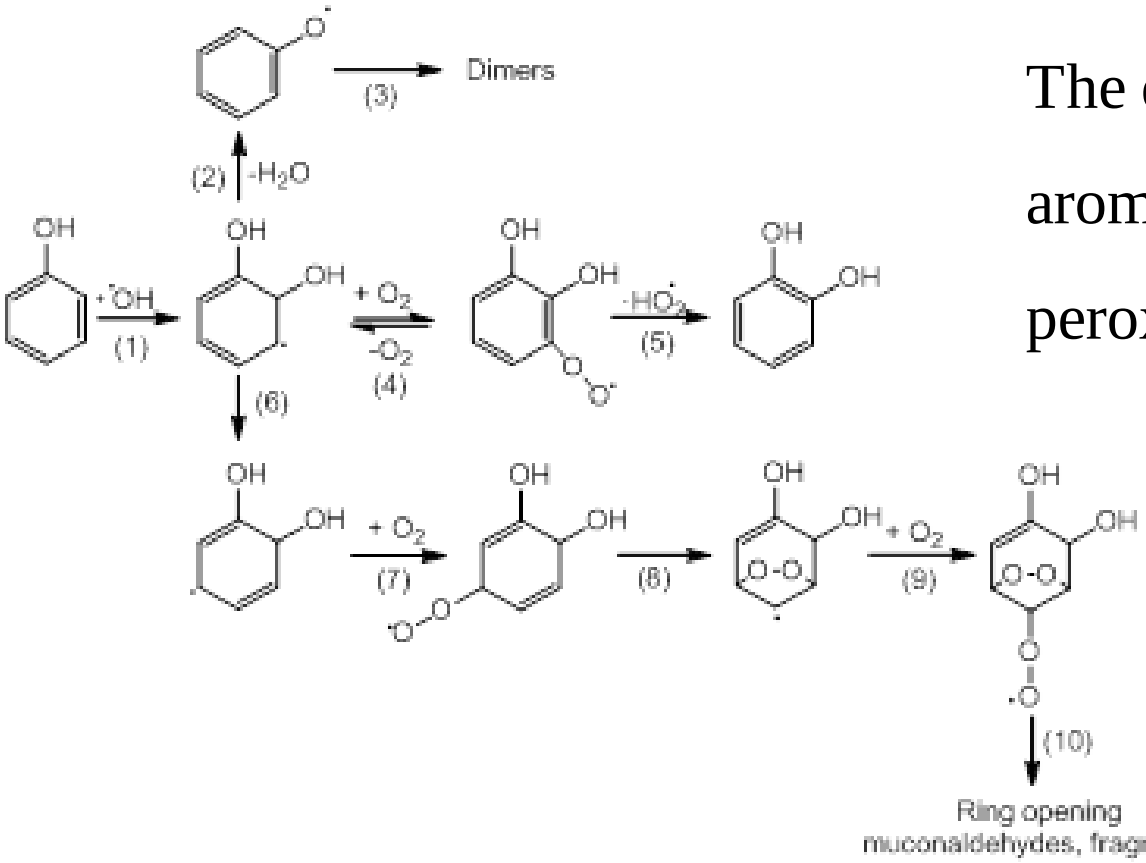
In aerated solutions $e_{aq}^{\bullet -}$ and $H^{\bullet}$ disappear in reaction with dissolved O_2

$$e_{aq}^{\bullet -} + O_2 \longrightarrow O_2^{\bullet -} \qquad k = 1.9 \times 10^{10}\ mol^{-1}\ dm^3\ s^{-1}$$

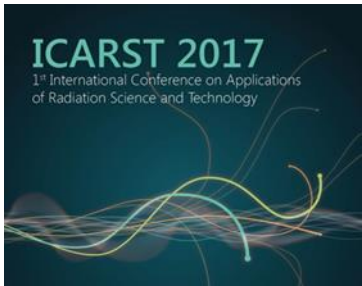
$$H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet} \qquad k = 1.2 \times 10^{10}\ mol^{-1}\ dm^3\ s^{-1}$$



Reaction of oxidizing radical (e.g. •OH) with organic molecule brings about one-electron oxidation, second oxidation occurs when the radical reacts with O_2. Further oxidations through peroxyl radicals. In reducing radical reactions carbon centered radical reacting with O_2 starts oxidative degradation. Both oxidizing and reducing radicals lead to oxidative degradation.



The degradation of the aromatic ring occurs in peroxyl radical reactions.

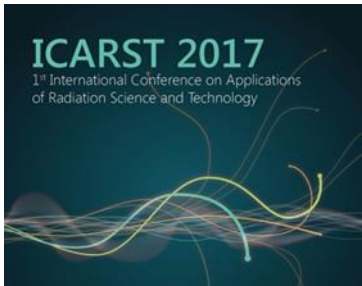


Reactions of reactive radicals with water constituents

During practical water (potable or wastewater) irradiations dissolved O_2, Cl^-, HCO_3^-/CO_3^{2-} and the dissolved organic carbon DOC consumes most part of primary water radiolysis radical intermediates. The Cl^-, HCO_3^-/CO_3^{2-} and DOC concentrations vary in wide ranges:

Cl^-	10^{-4} - 10^{-3} mol dm^{-3}
HCO_3^-/CO_3^{2-}	10^{-3} - 10^{-2} mol dm^{-3}
DOC	2 – 100 mg dm^{-3}

(The organic content of drinking water, water of lakes and rivers is referred to as dissolved organic carbon. DOC mainly consists of fulvic and humic acids).



Reactions of •OH with the main constituents of a model purified water leaving a WWTP

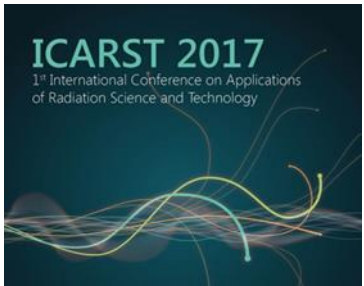
Species	Concentration	k, mol^{-1} dm^3 s^{-1}	Reaction, % Low pH	Reaction, % Neutral pH
Cl^-	5×10^{-4} mol dm^{-3}	4.3×10^9	81	
HCO_3^-	1×10^{-2} mol dm^{-3}	8.5×10^6	3.8	18
DOC	20 mgC dm^{-3}	$2 \times 10^{4*}$	15	81
PhX	1×10^{-6} mol dm^{-3}	5×10^9	0.2	1

* mgC^{-1} dm^3 s^{-1}

Reactions of $SO_4^{\bullet-}$ with the main constituents of a model purified water leaving a WWTP

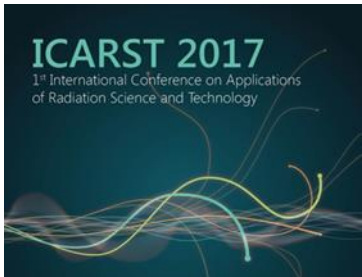
Species	Concentration	k, mol^{-1} dm^3 s^{-1}	Reaction, %
Cl^-	5×10^{-4} mol dm^{-3}	3.2×10^8	50
HCO_3^-	1×10^{-2} mol dm^{-3}	5×10^6	16
DOC	20 mgC dm^{-3}	$5.3 \times 10^{3*}$	33
PhX	1×10^{-6} mol dm^{-3}	3×10^9	1

* mgC^{-1} dm^3 s^{-1}



Conclusions:

1. $^{\bullet}OH$ is a selective radical in addition and abstraction. Reactions are never diffusion controlled, chemical reactivity plays important role.
2. The rate constants with several classes of organic molecules are very low. $^{\bullet}OH$ cannot degrade these pollutants.
3. Reductive radicals, $e_{aq}^{\bullet-}$ and $H^{\bullet}$ also contribute to oxidative degradation.
4. In practical water matrices $^{\bullet}OH$ mostly reacts with Cl^-, HCO_3^-/CO_3^{2-} DOC, less than 1% is utilized for degradation of target compounds.
5. Secondary radicals formed in reactions with Cl^-, HCO_3^-/CO_3^{2-} and DOC are more selective than $^{\bullet}OH$ and contribute to the degradation.
6. The dissolved O_2 concentration strongly influences the rate.
7. In surface waters $CO_3^{\bullet-}$ is the most abundant radical which strongly influences the degradation of harmful pollutants.



Some of the old ideas should be reconsidered

We have to do up the buttons again.

Thank you for your attention