Hydroxyl radical induced degradation of aromatic molecules

Poorest source of hydroxyl radical

Radiolysis of water

$$H_2O \longrightarrow H_2O^{+\bullet} + e^{-\bullet}$$

$$H_2O \longrightarrow H_2O^*$$

$$H_2O^{+\bullet} + H_2O \longrightarrow H_3O^+ + {}^\bullet OH$$

$$e^{-\bullet} + nH_2O \longrightarrow e_{aq}^{-\bullet}$$

$$H_2O^* \longrightarrow {}^\bullet OH + H^\bullet$$

$$e_{aq}^{-\bullet} + H_3O^+ \longrightarrow H^\bullet + H_2O$$

$$k = 2.3\times10^{10}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$$

Hydroxyl radical, properties

- The $^{\bullet}OH$ is oxidizing radical. Reduction potential: 1.9 V

- In N_2O saturated solution the yield of $^{\bullet}OH$ reacting with solute of 10^{-3} mol dm^{-3} concentration $G \approx 0.56$ μmol J^{-1}. $H^{\bullet}$ contributes to reactions with a yield 0.057 μmol J^{-1}.

$$N_2O + e_{aq}^{-\bullet} + H_2O \longrightarrow N_2 + OH^- + {}^{\bullet}OH$$

$$k = 7\times10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

- In alkaline solution $^{\bullet}OH$ converts to $O^{-\bullet}$ ion with a pK_a of 11.9:

$$^{\bullet}OH + OH^- \longrightarrow O^{-\bullet} + H_2O$$

$$k = 1.3\times10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

- Light absorption of $^{\bullet}OH$ is below 220 nm.

$OH^{\bullet}$ + aromatic molecule reaction

- **Direct oxidation**

$$^{\bullet}OH + C_6H_5OH \longrightarrow C_6H_5O^{\bullet} + H_2O$$
$$^{\bullet}OH + C_6H_5O^{-} \longrightarrow C_6H_5O^{\bullet} + OH^{-}$$

- **Addition forming hydroxycyclohexadienyl radical**

$$^{\bullet}OH + C_6H_5OH \longrightarrow {}^{\bullet}OHC_6H_5OH$$

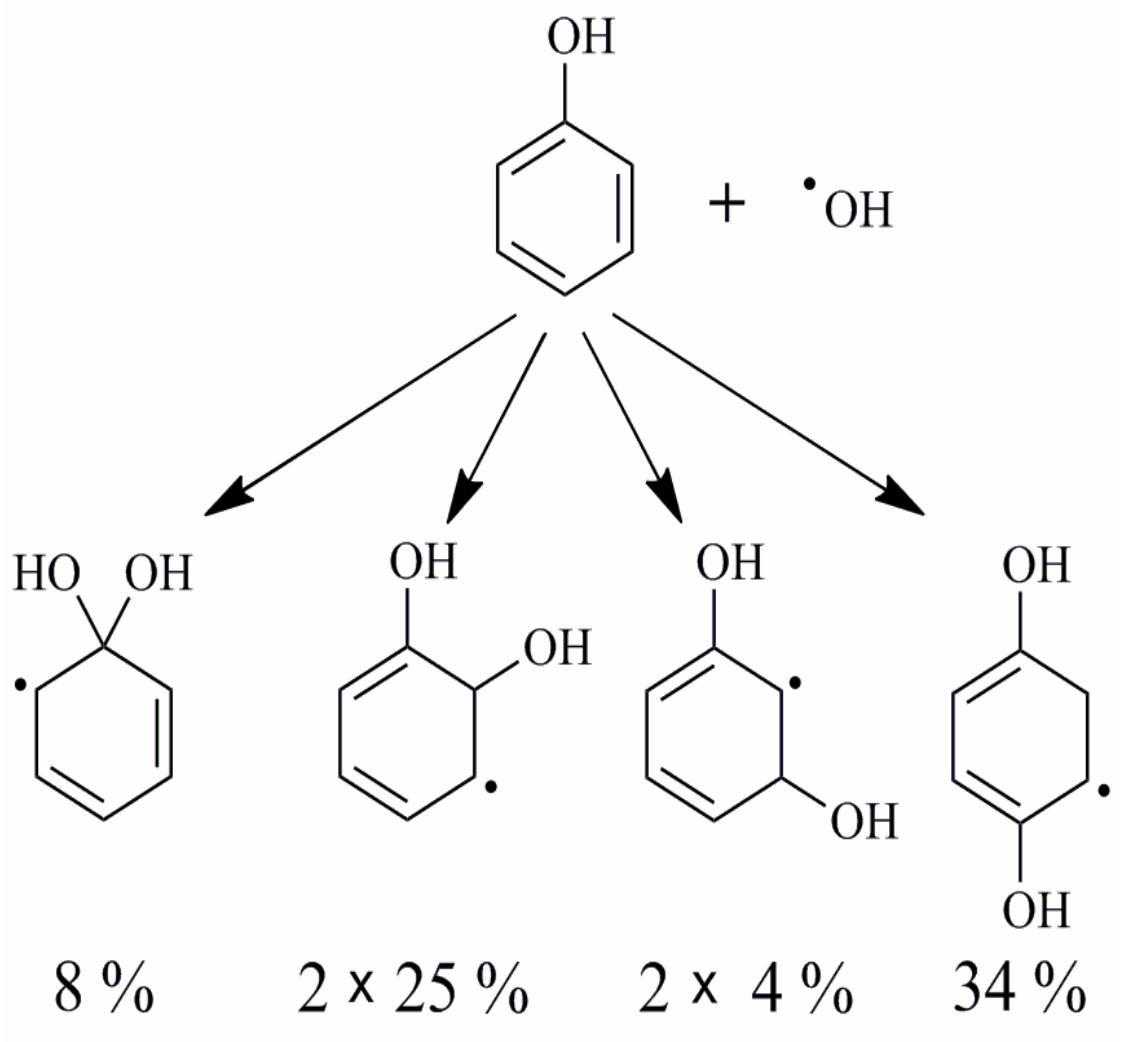
- **H-atom abstraction from side chain**

$$^{\bullet}OH + CH_3C_6H_5 \longrightarrow {}^{\bullet}CH_2C_6H_5 + H_2O$$

Aromatic molecule + $^{\bullet}OH$ reaction is dominated by addition

- OH addition to phenol

Monitoring charge distribution



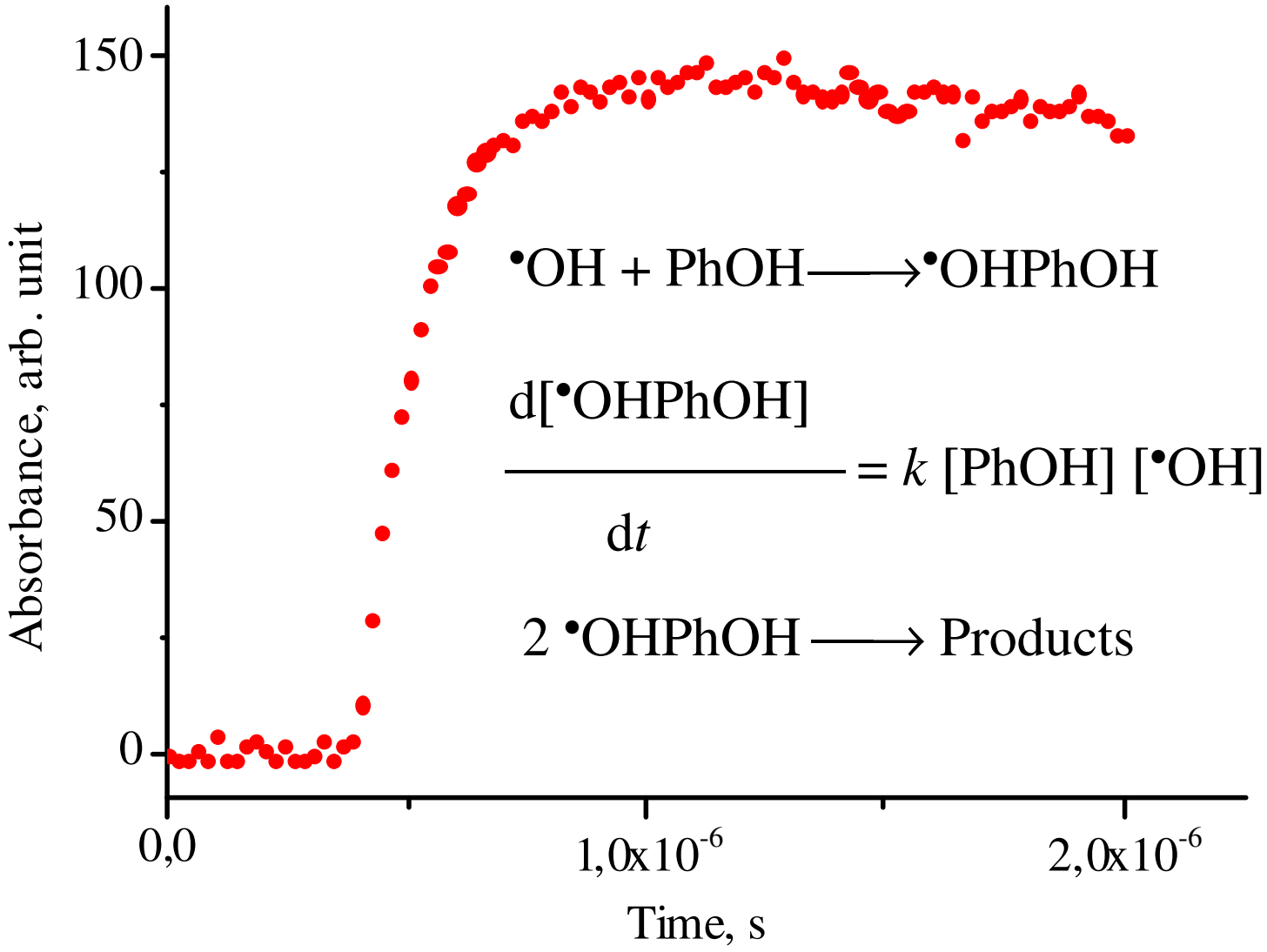
Methods of rate coefficient determination

Direct method, build-up measurement

„When the signal growth is followed by rapid decay one tends to underestimate the initial reaction period and as a result overestimate the rate coefficient. The unrealistic rate coefficients, e.g. those which are much higher than the diffusion limited rate coefficient, given in number of cases for reaction of $^{\bullet}OH$ with phenols, are suggested for re-evaluation."

(Schuler R.H., Albarran, G., 2002. Radiat. Phys. Chem. 64, 189–195).

Rate coefficient determination by build-up



Rate coefficient determination by build-up

$$^{\bullet}OH + PhOH \longrightarrow {}^{\bullet}OHPhOH$$

$$\frac{d[^{\bullet}OH]}{dt} = -k\,[PhOH]\,[^{\bullet}OH] = -k'\,[^{\bullet}OH] \longrightarrow [^{\bullet}OH] = [^{\bullet}OH]_0\, e^{-k't}$$

$$\frac{d[^{\bullet}OHPhOH]}{dt} = k'\,[^{\bullet}OH] = k'\,[^{\bullet}OH]_0\, e^{-k't}$$

$$[^{\bullet}OHPhOH] = [^{\bullet}OH]_0\,(1 - e^{-k't}) = [\,^{\bullet}OHPhOH\,]_{\infty}\,(1 - e^{-k't})$$

$$A_{^{\bullet}OHPhOH} = A_{^{\bullet}OHPhOH}\,(1 - e^{-k't})$$

$$2\ ^{\bullet}OHPhOH \longrightarrow \text{Products}$$

Methods of rate coefficient determination

•Pulse radiolysis with competitive technique

Thiocianate

$$^{\bullet}OH + SCN^- \xrightarrow{k_{20}} OH^- + SCN^{\bullet} \qquad 1.1 \times 10^{10}\ mol^{-1}\ dm^3\ s^{-1}$$

$$SCN^{\bullet} + SCN^- \longrightarrow (SCN)_2^{-\bullet} \qquad \varepsilon_{500\ nm} = 7100\ mol^{-1}\ dm^3\ cm^{-1}$$

$$OH + S \xrightarrow{k_{49}} OHS^{\bullet}$$

$$\frac{1}{[(SCN)_2^{-\bullet}]} = \frac{1}{[(SCN)_2^{-\bullet}]_0} + \frac{1}{[(SCN)_2^{-\bullet}]_0} \frac{k_{49}}{k_{20}} \frac{[S]}{[SCN^-]}$$

Ethanol

$$C_2H_5OH + {}^{\bullet}OH \longrightarrow C_2H_4{}^{\bullet}OH + H_2O \qquad 1.9 \times 10^9\ mol^{-1}\ dm^3\ s^{-1}$$

Ferrocyanide

$$^{\bullet}OH + [Fe(CN)_6]^{4-} \longrightarrow OH^- + [Fe(CN)_6]^{3-} \qquad 9.3 \times 10^9\ mol^{-1}\ dm^3\ s^{-1}$$

$$\lambda_{max} = 410\ nm,\ \varepsilon_{max} = 1000\ mol^{-1}\ dm^3\ cm^{-1}$$

Wilson, R.L., Greenstock, C.L., Adams, G.E., Wageman, R., Dorfman, L.M., 1971. Int. J. Radiat. Phys. Chem. 3, 211–220.

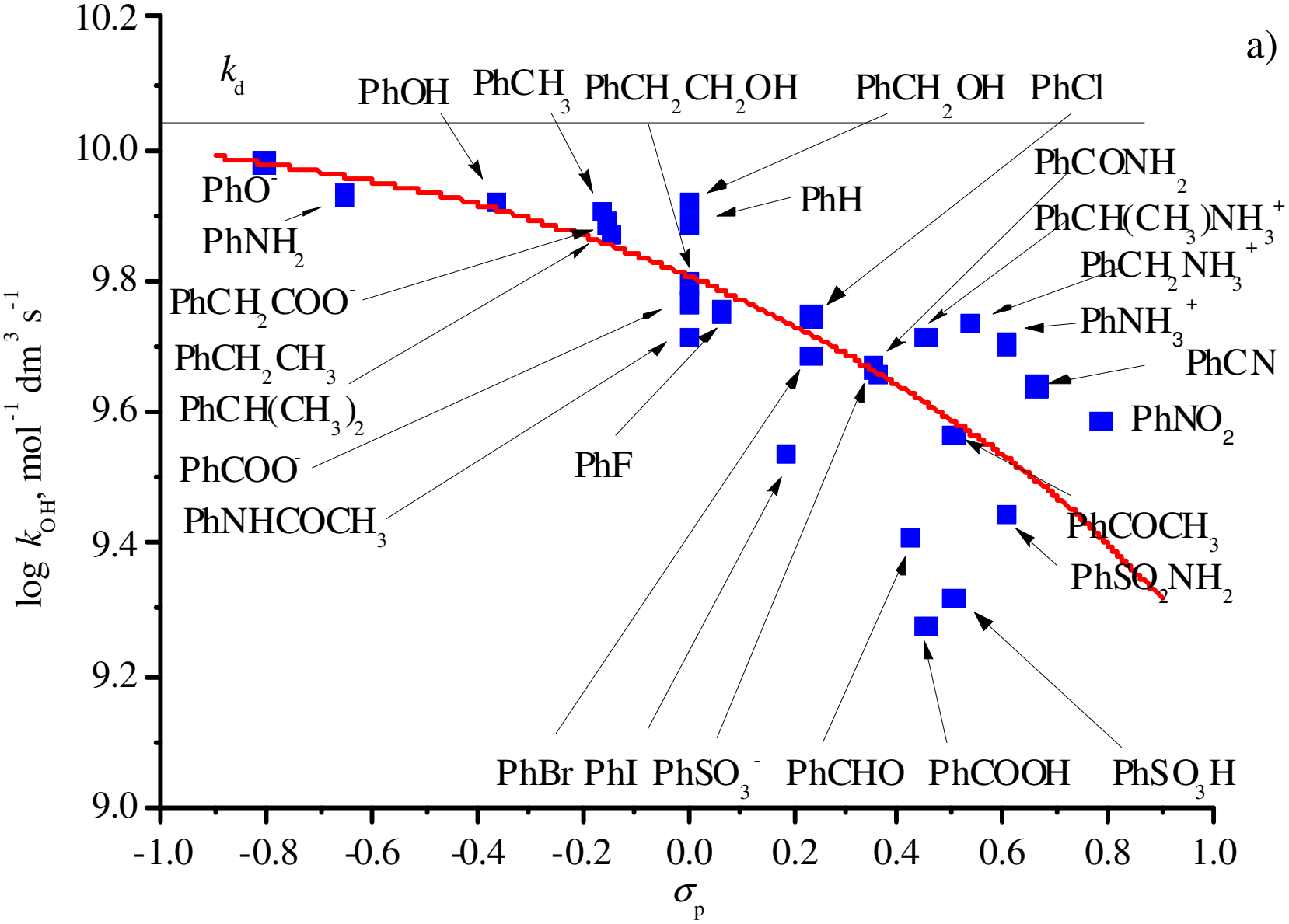
Methods of rate coefficient determination

•Competitive technique using final product measurement

The method using steady-state gamma radiolysis and competition with selected compound often gives good agreement in the rate coefficient with the ones determined by direct method. For the good agreement application of low conversion is needed.

In rate coefficient determinations for hydroxyl radical generation sometimes Fenton reaction is used, the rate coefficient is obtained by a competitive technique. The Fenton system is rather complex, the results should be considered with some care.

Structure dependence of rate coefficients •OH + Mono-substituted aromatics



Hammett substituent constants

The values of σ are defined from the ionization constants of benzoic acids:

$$\sigma = \log K_X - \log K_H$$

Where K_H is the ionization constant for benzoic acid in water (4.29) at 25 °C and K_X is the corresponding constant for *meta*- or *para*-substituted benzoic acids.

The diffusion controlled rate coefficient:

$$k_{\text{diff}} = 4\,\pi\,(D_{\text{PhX}} + D_{\text{OH}})\,(r_{\text{PhX}} + r_{\text{OH}})\,N \times 10^3 \quad (\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1})$$

D_{PhX} and D_{OH} diffusion coefficients in $\text{m}^2\ \text{s}^{-1}$

r_{PhX} and r_{OH} are the reaction radii

N is the Avogaro's number

$k_{\text{diff}} \approx 1.1 \times 10^{10}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$

	r_{OH}, x 10^9 m	r_{PhX}, x 10^9 m	D_{OH}, $\text{m}^2\ \text{s}^{-1}$	D_{PhX}, $\text{m}^2\ \text{s}^{-1}$
Benzene	0.22	0.33	2.31×10^{-9}	1.4×10^{-9}
Chlorobenzene		0.35		0.4×10^{-9}
Phenol		0.35		0.4×10^{-9}

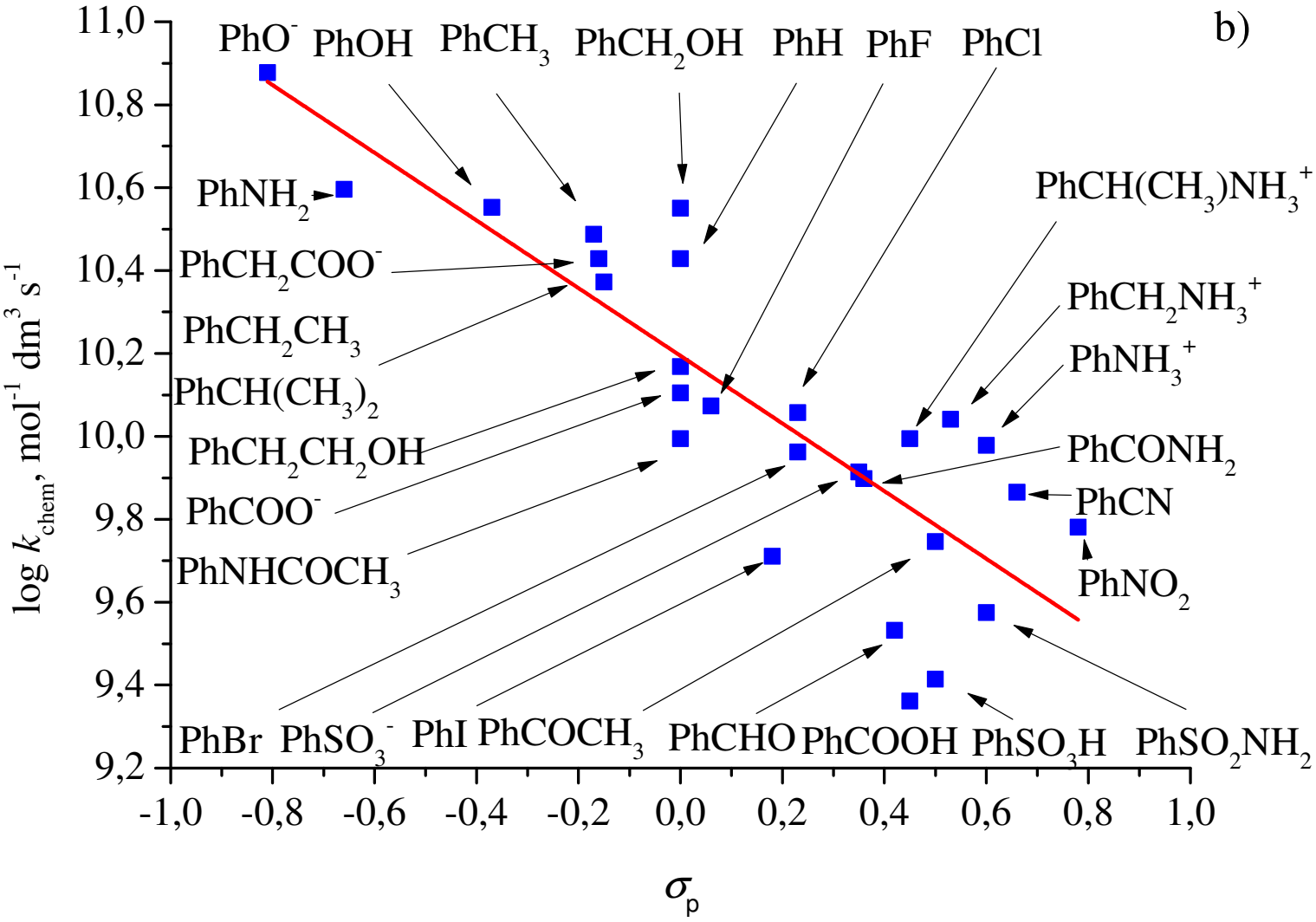
Ashton, L., Buxton, G.V.; Stuart, C.R., 1995. J. Chem. Soc., Faraday Trans. 91, 1631–1633. Wojnárovits L., 1984. J. Photochem. 24, 341–353.

Separation of diffusion and chemical reaction controlled rate coefficients

$$1/k_{OH} = 1/k_{diff} + 1/k_{chem}$$

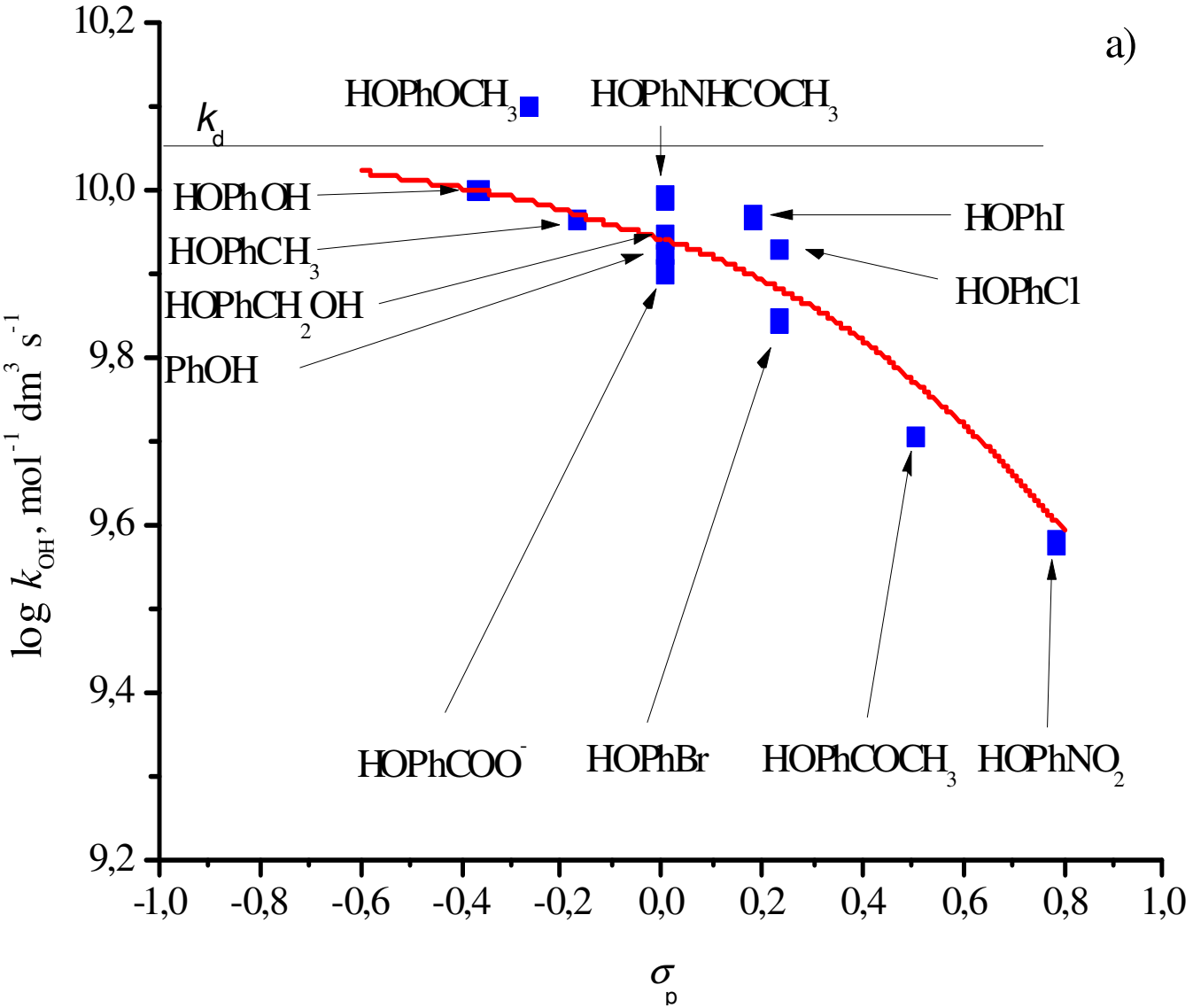
k_{OH}, $mol^{-1}\ dm^3\ s^{-1}$	k_{diff}, $mol^{-1}\ dm^3\ s^{-1}$	k_{chem}, $mol^{-1}\ dm^3\ s^{-1}$
0.2×10^{10}	1.1×10^{10}	0.24×10^{10}
0.4×10^{10}		0.63×10^{10}
0.6×10^{10}		1.3×10^{10}
0.8×10^{10}		2.9×10^{10}
1.0×10^{10}		1.1×10^{11}

Structure dependence of rate coefficients •OH + Mono-substituted aromatics



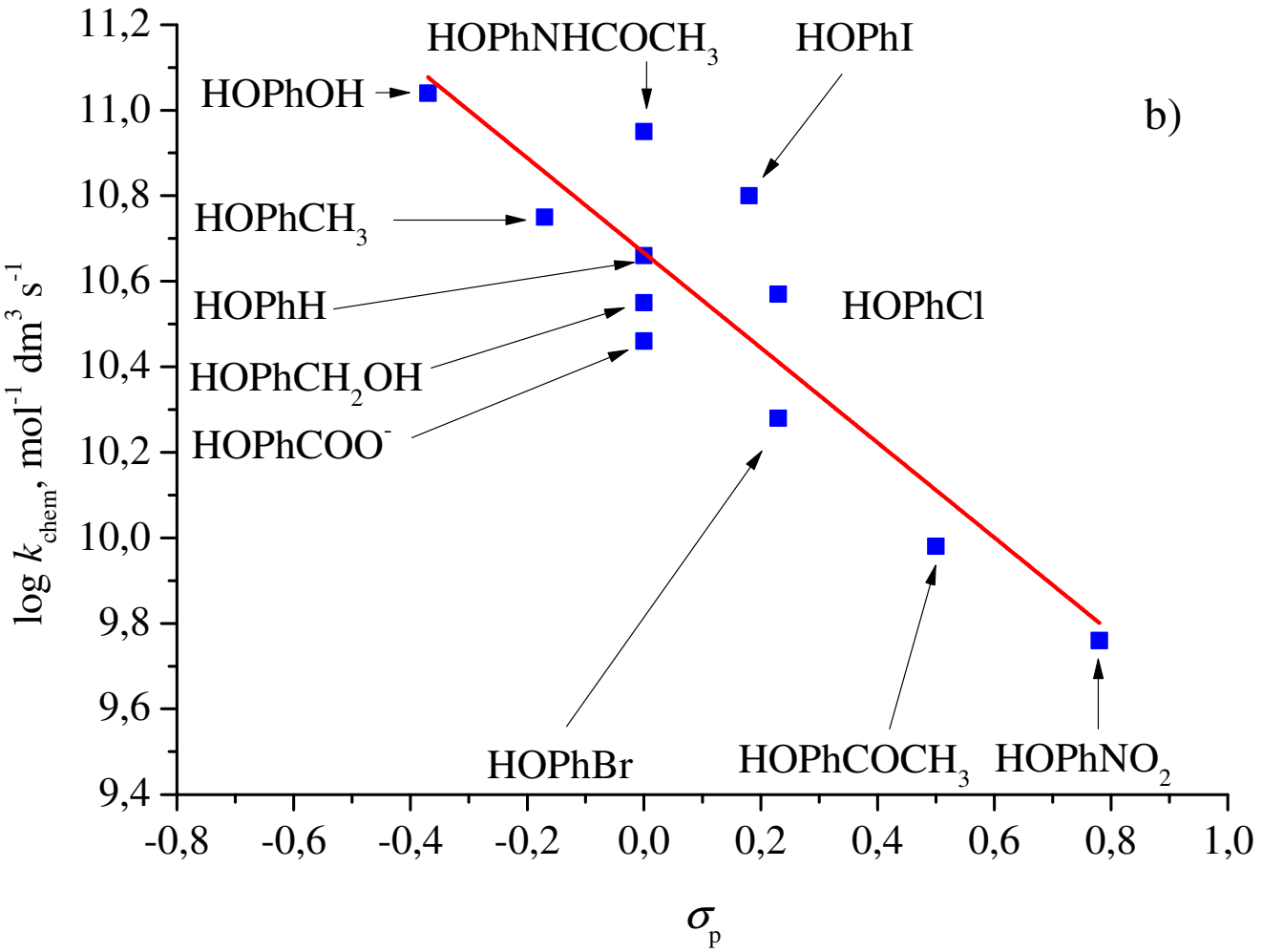
Structure dependence of rate coefficients

•OH+ *p*-substituted phenols

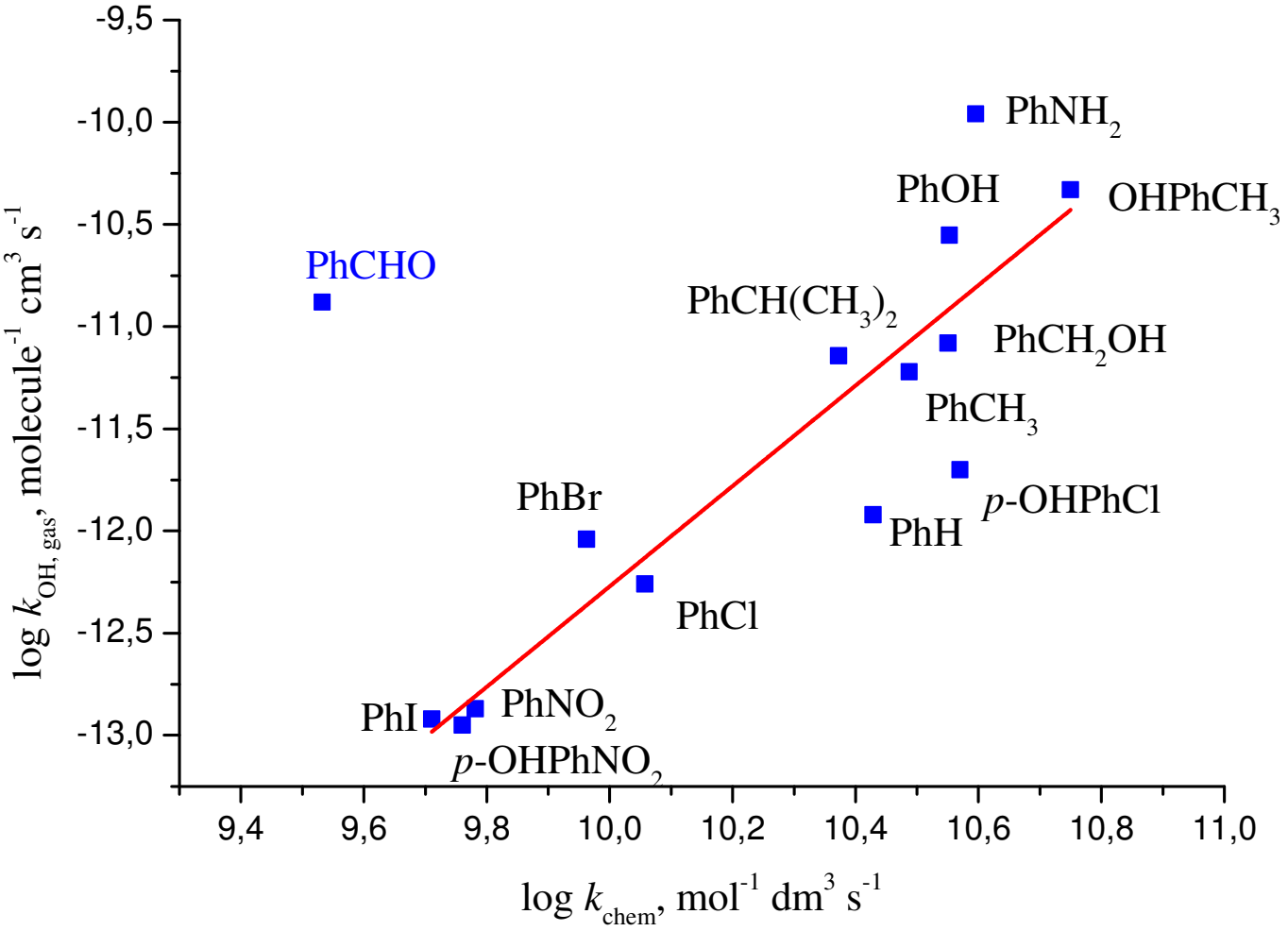


Structure dependence of rate coefficients

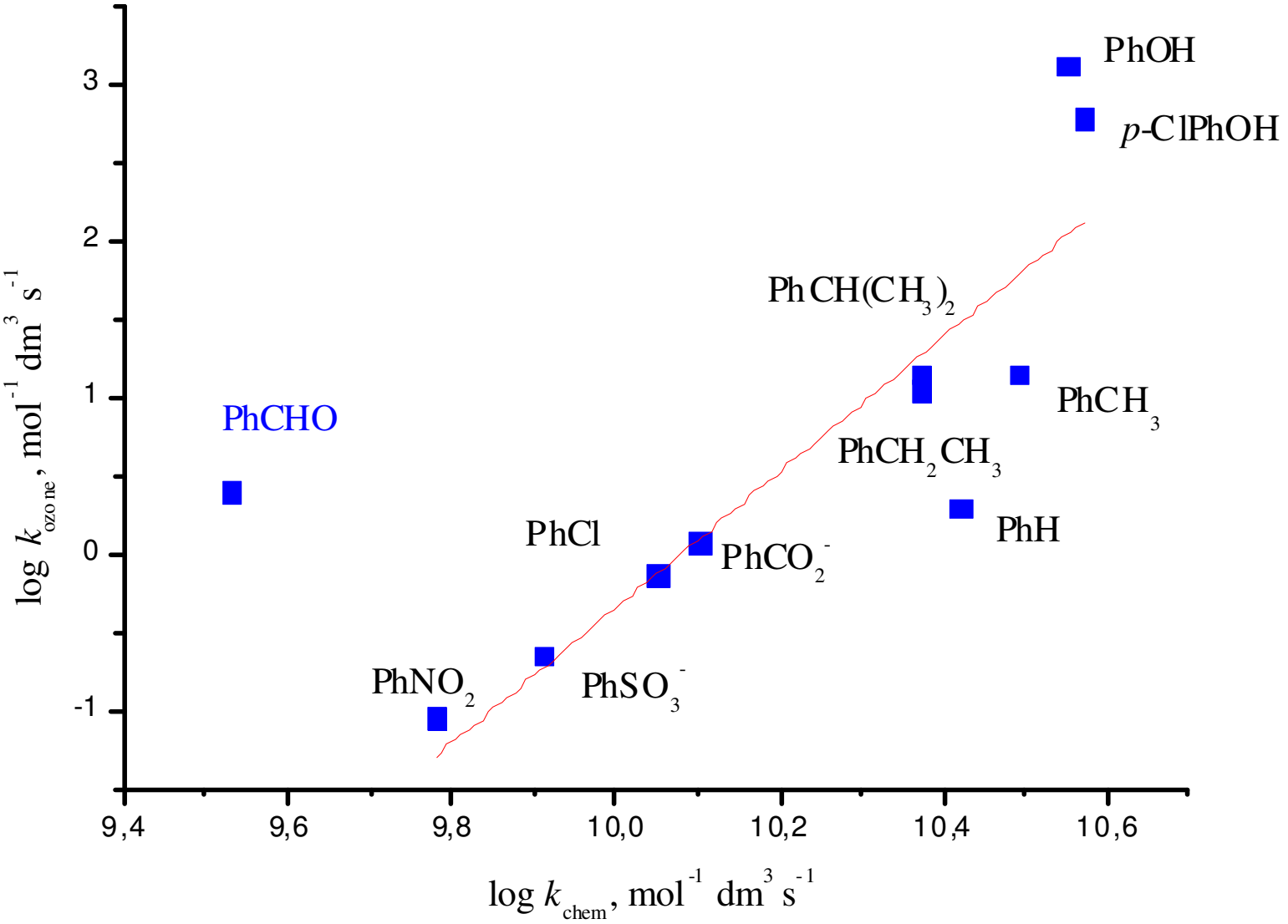
•OH + *p*-substituted phenols



Comparison of •OH reaction with aromatic molecules in gas and liquid phases



Comparison of aromatic molecule reaction with $^{\bullet}OH$ and O_3



Conclusion

-The k_{OH}'s fall in the range 2×10^9 mol^{-1} dm^3 s^{-1} – 1×10^{10} mol^{-1} dm^3 s^{-1}, the highest values approach the diffusion controlled limit, ~1.1×10^{10} mol^{-1} dm^3 s^{-1}.

-By plotting k_{OH}'s as a function of Hammett constants we do not obtain straight lines, due to the partially diffusion controlled character of the reaction.

-The log k_{chem}'s calculated by the Noyes equation, are linearly correlated with the Hammett constants.

-The structure dependence of the electrophile $^{\bullet}OH$ + aromatic molecule reaction can be interpreted in terms of electron donating and withdrawing substituent.

·OH reaction with aromatic molecules

- Reaction without "stable" intermediate complex

$$PhX + {}^{\bullet}OH \rightleftarrows [PhX + {}^{\bullet}OH] \rightarrow \sigma\text{-}PhXOH^{\bullet}$$

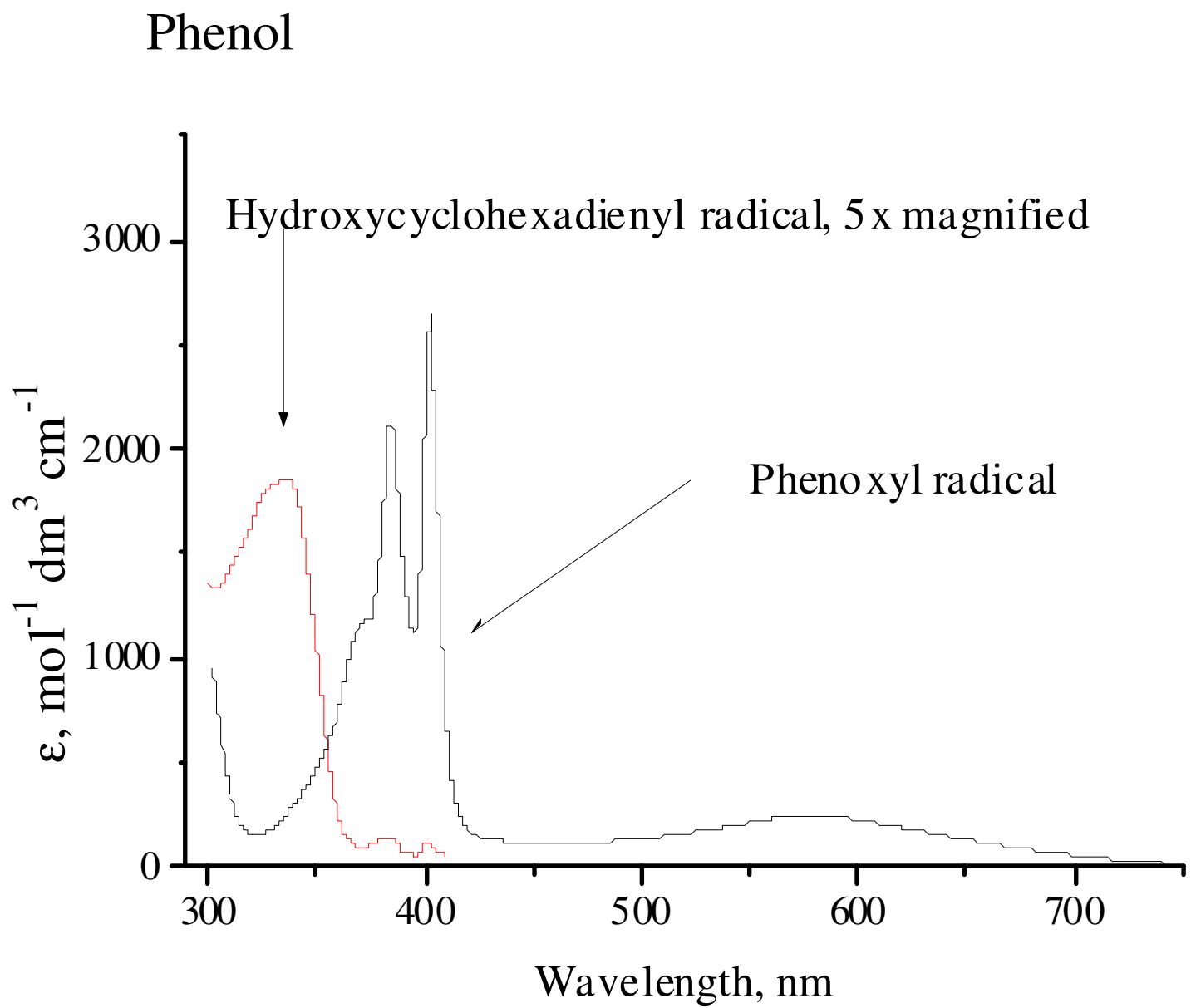
- Reaction with "stable" intermediate complex

$$PhX + {}^{\bullet}OH \underset{k_2}{\overset{k_1}{\rightleftarrows}} [\pi\text{-}PhXOH^{\bullet}] \xrightarrow{k_3} \sigma\text{-}PhXOH^{\bullet}$$

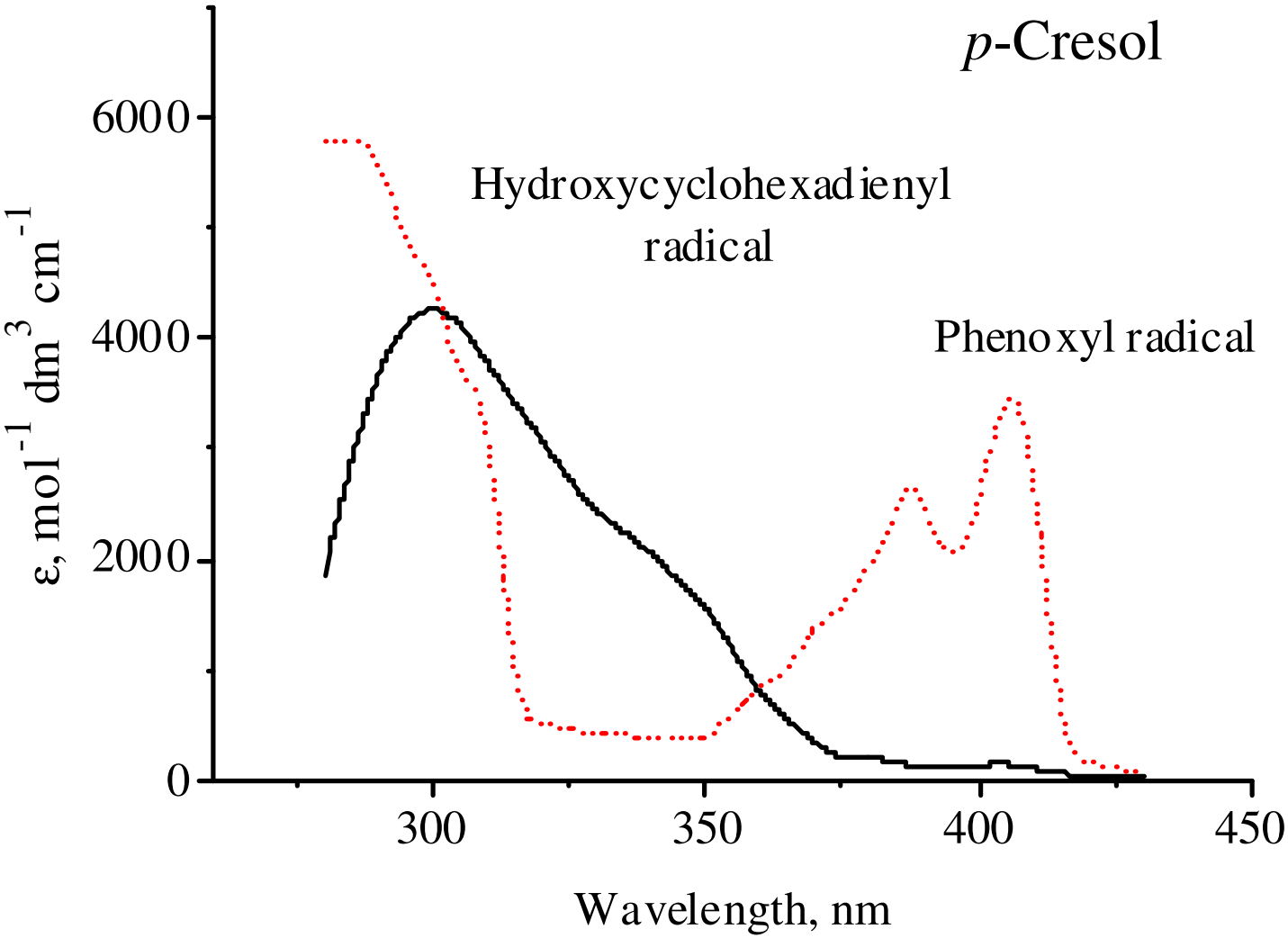
$$[\sigma\text{-}PhXOH^{\bullet}] = \frac{l_1\,[{}^{\bullet}OH]\,e^{-l2\,t}}{l_2 - l_1} - \frac{l_2\,[{}^{\bullet}OH]\,e^{-l1\,t}}{l_2 - l_1} + [{}^{\bullet}OH]$$

$$k_1 + k_2 + k_3 = l_1 + l_2 \qquad k_1 \times k_3 = l_1 \times l_2$$

Hydroxycyclohexadienyl ⟶ phenoxyl transition



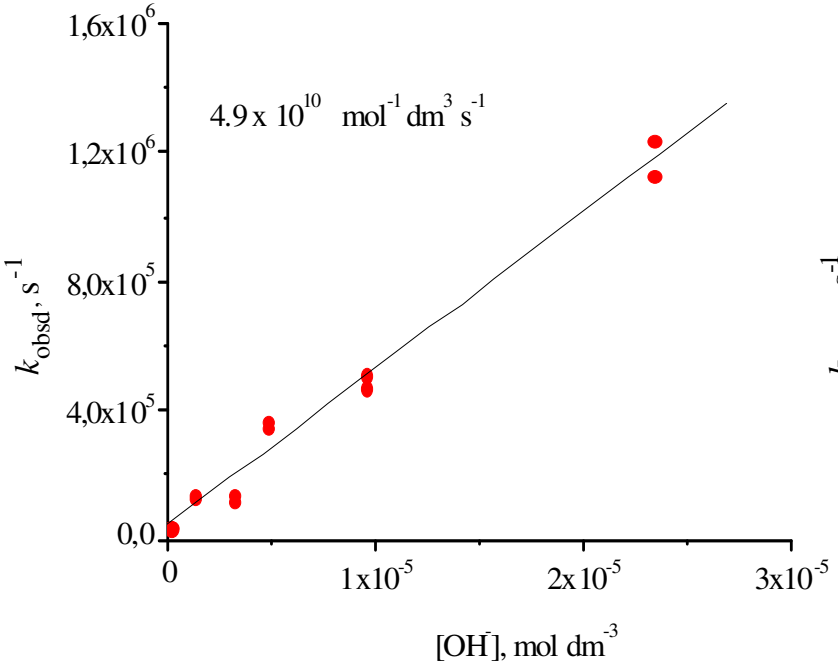
Hydroxycyclohexadienyl ⟶ phenoxyl transition

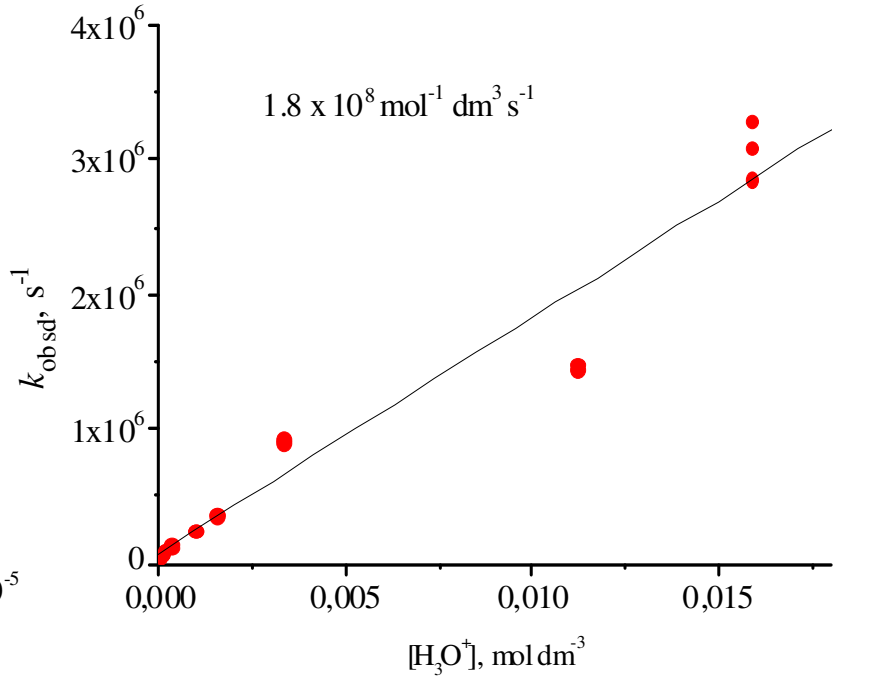


Acid-base catalyzed water elimination from the adduct

$OH^- + p\text{-}CH_3C_6H_4(OH)_2^\bullet \longrightarrow p\text{-}CH_3C_6H_4O^\bullet + H_2O + OH^-$

$H_3O^+ + p\text{-}CH_3C_6H_4(OH)_2^\bullet \longrightarrow p\text{-}CH_3C_6H_4O^\bullet + H_2O + H_3O^+$





Peroxy radical forming reaction

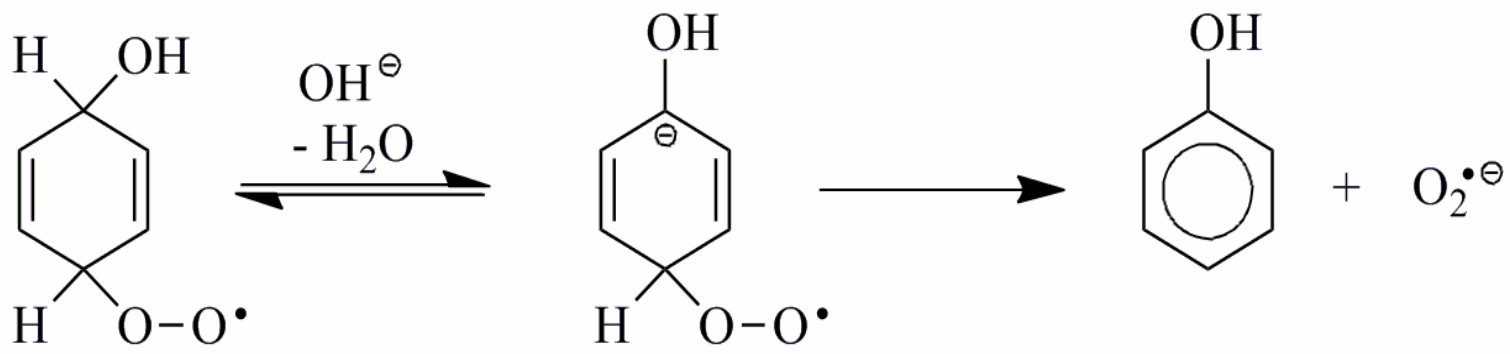
$$^{\bullet}OHPhOH + O_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} OHPh(OH)OO^{\bullet} \longrightarrow \text{Products}$$

- Spin selectivity question
- R-OO$^{\bullet}$ bond energy is in the 25 kJ mol^{-1} range, reversibility
- Rate coefficients for forward and backward reactions strongly depend on the electron density on the ring
- Peroxy radicals have light absorption below 300 nm

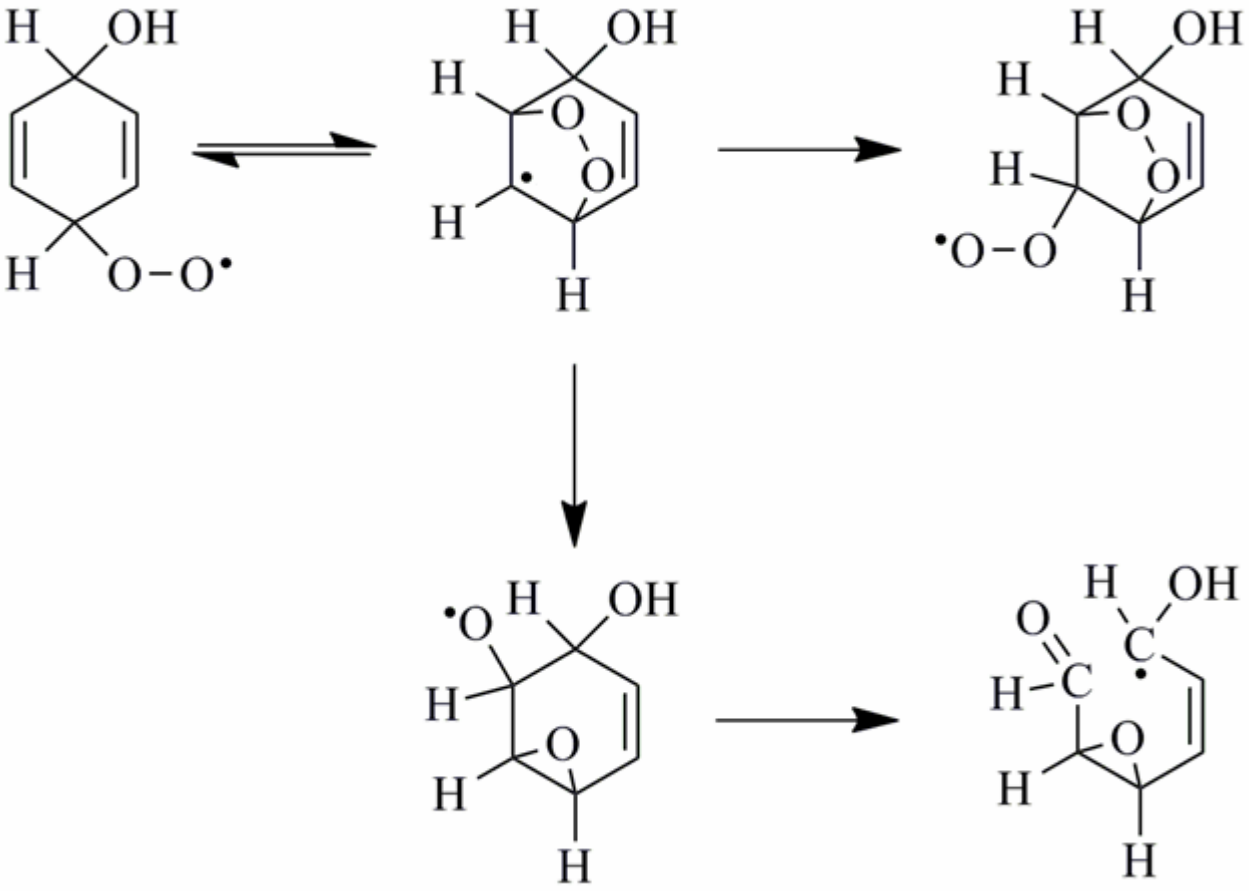
Peroxy radical forming reaction

Aromatic molecule	k_f, $mol^{-1}\ dm^3\ s^{-1}$	k_r, s^{-1}	K, $mol^{-1}\ dm^3$
Anisol	8×10^8	3.9×10^4	2.1×10^4
Toluene	4.8×10^8	7.5×10^4	0.64×10^4
Fluorobenzene	4.6×10^8	5.5×10^4	0.84×10^4
Benzene	3.1×10^8	1.2×10^4	2.6×10^4
Chlorobenzene	2.6×10^8	5.5×10^4	0.47×10^4
Benzoic acid ion	2.0×10^8	1.3×10^4	1.5×10^4

$HO_2^{\bullet}$ and $O_2^{-\bullet}$ eliminations from peroxy radicals



Endoperoxide formation, ring opening



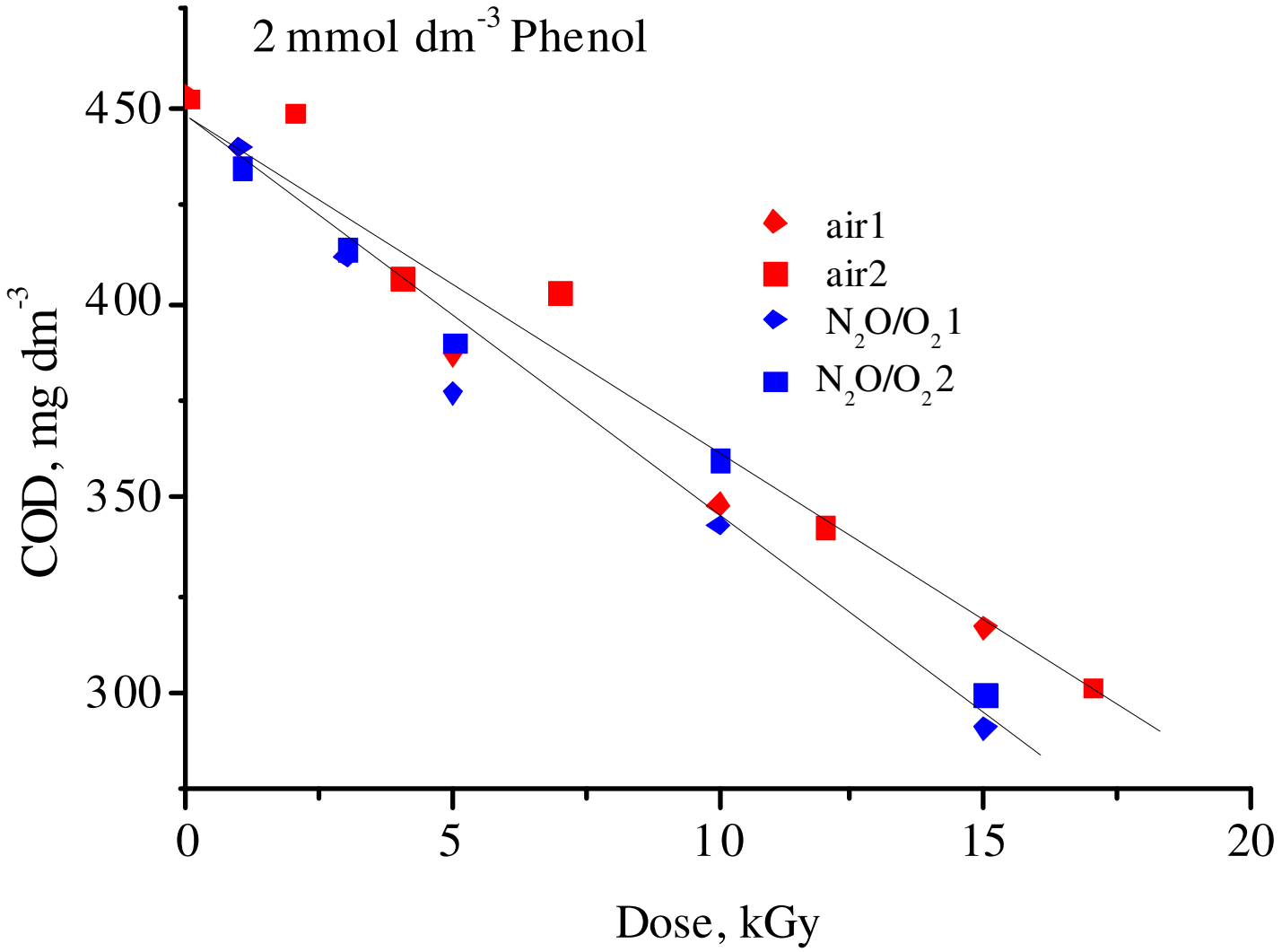
Oxygen consumption measurements

Oxygen selective electrode

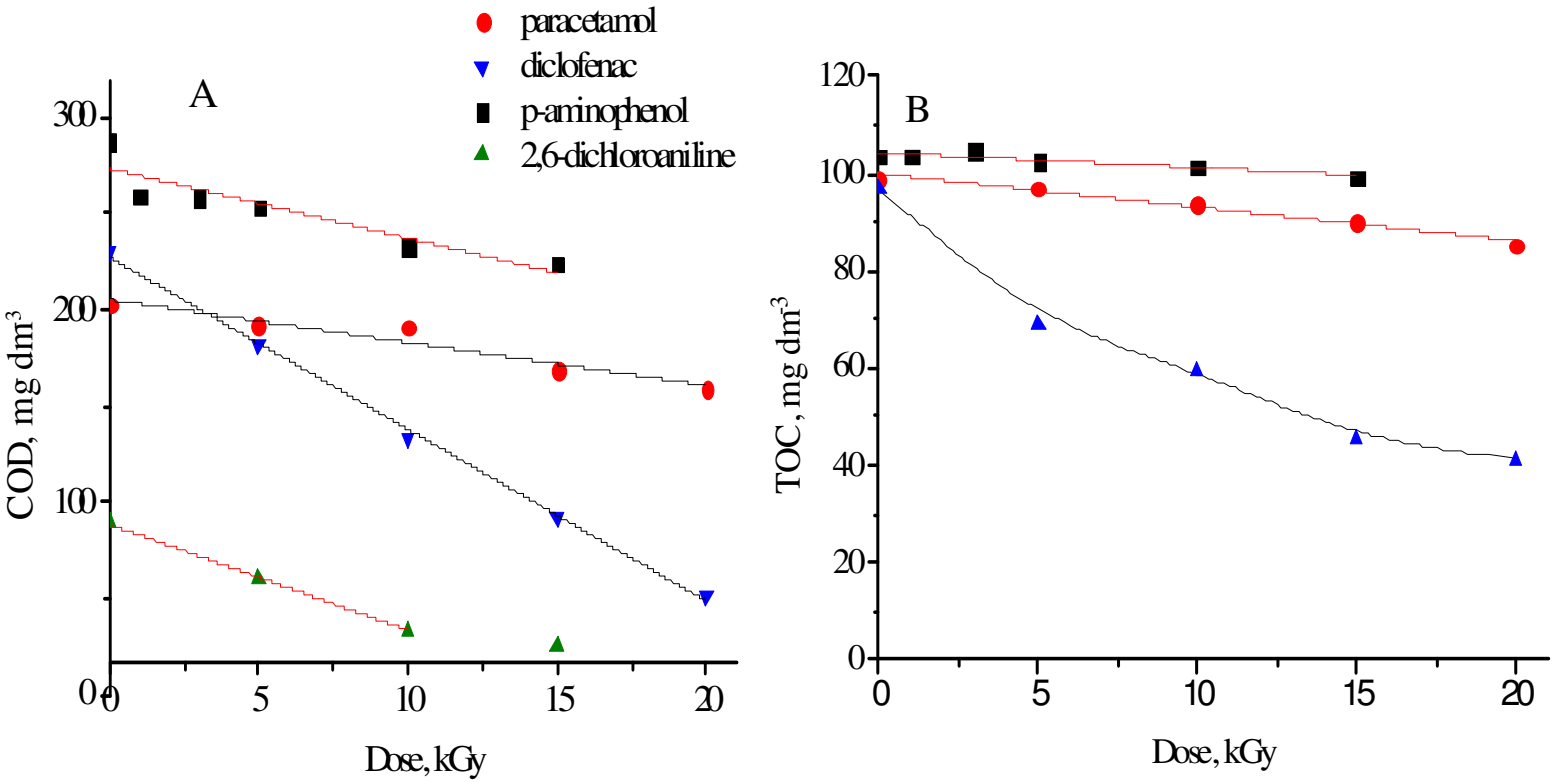
Efficiency: O_2 molecule consumed/•OH introduced

Compound	Efficiency
Formate	0.55
Isopropanol	0.55
t-Butanol	0.80
Diethyl ether	0.84

Dose dependence of Chemical Oxygen Demand



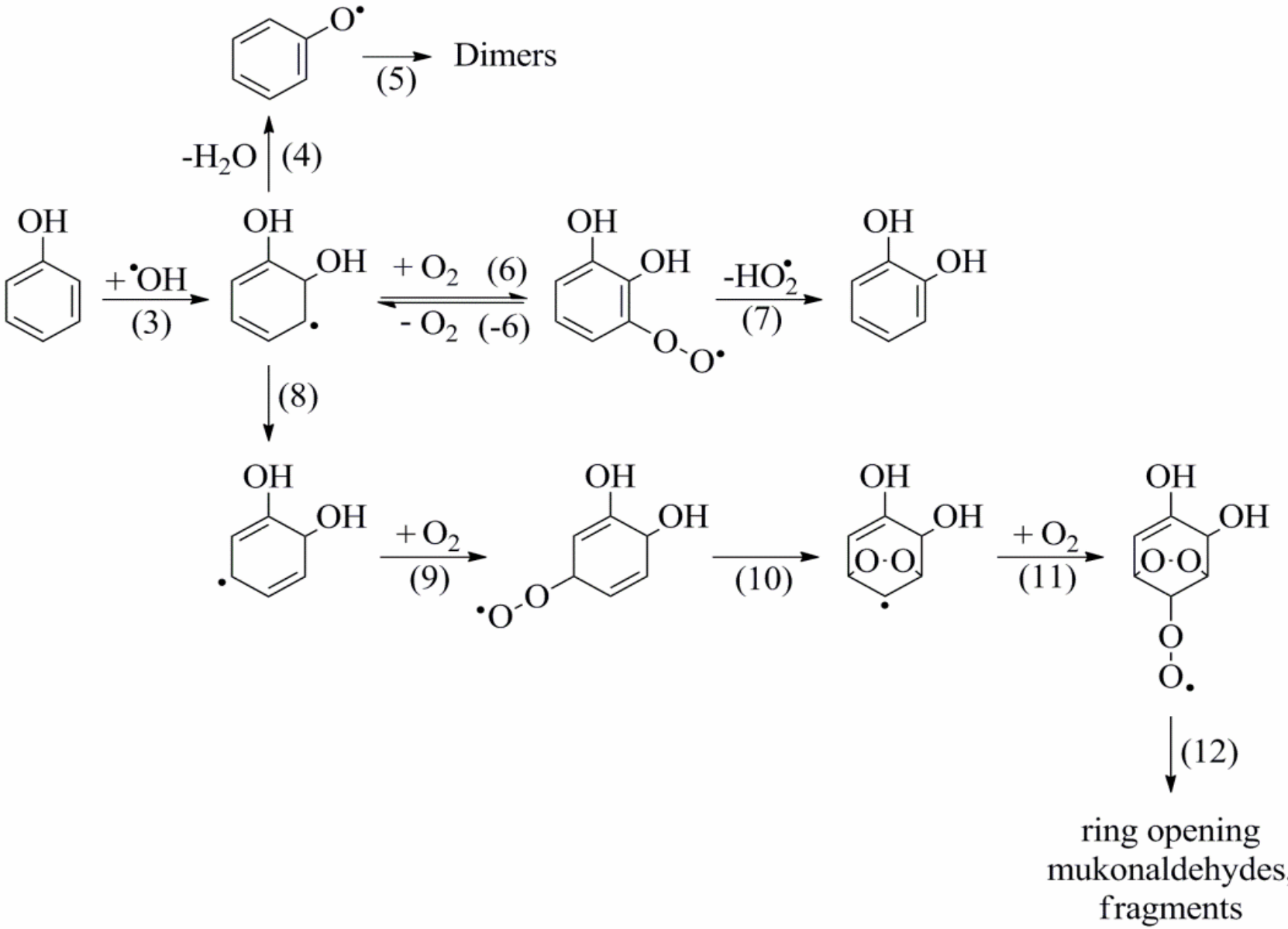
Connection between Chemical Oxygen Demand and Total Organic Carbon Content



Chemical Oxygen Demand

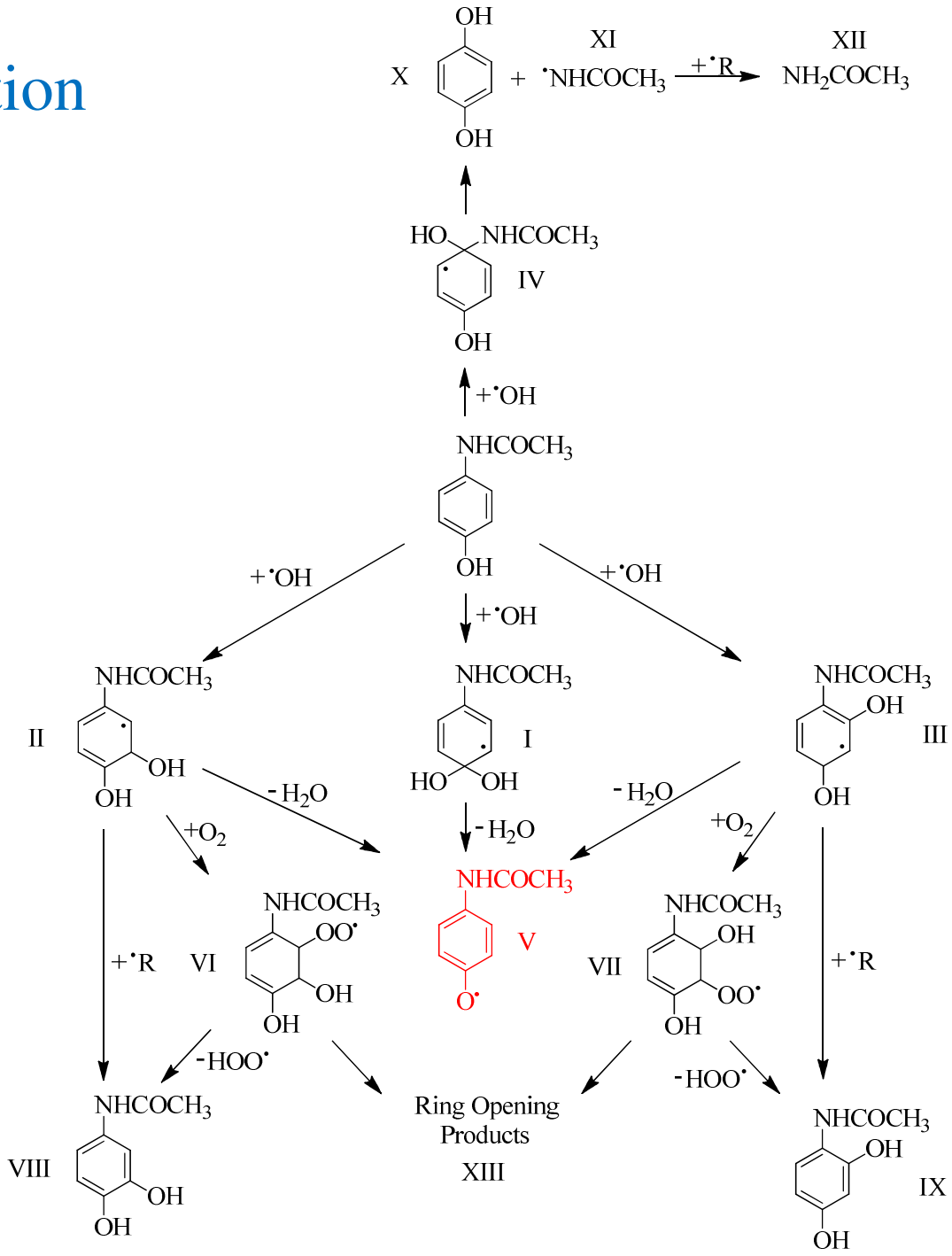
Compound	Slope, mg dm^{-3} kGy^{-1}	*E*
Phenol	8.8±0.6	0.98
o-, *m*-, *p*-Cresol	8.0±1.2	0.90
o-, *m*-, *p*-Chlorophenol	8.0±1.2	0.90
Ketoprofen	9.0±1.0	1.0
2,4-Dichlorophenoxy-acetic acid	8.0±0.5	0.9
Aspirin	8.1±0.5	0.9
Acetovanillone	6.9±0.4	0.77
Gallic acid	8.5±0.8	0.94
Maleic acid	7.4±0.7	0.82
Fumaric acid	9.0±0.7	1.0
Diclofenac	9.0±0.3	1.0
o-, *m*-, *p*-Aminophenol	4.0±1.2	0.45
Paracetamol	2.2±0.8	0.25
2,6-Dichloraniline	5.5±1.0	0.6
Acid Red 1	5.5±0.8	0.6

Phenol degradation



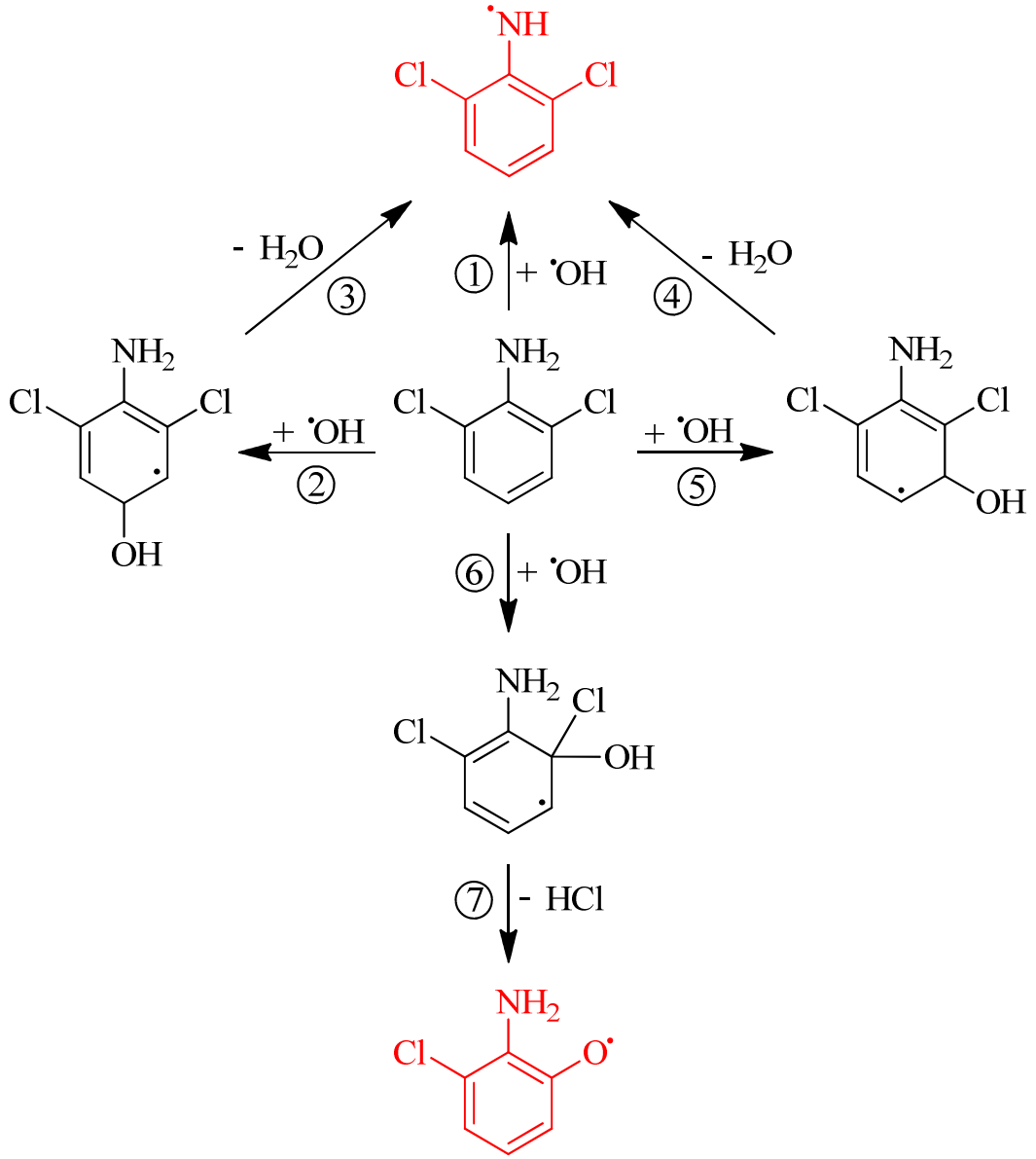
Paracetamol degradation

Phenoxyl (semi-iminoquinone) radical

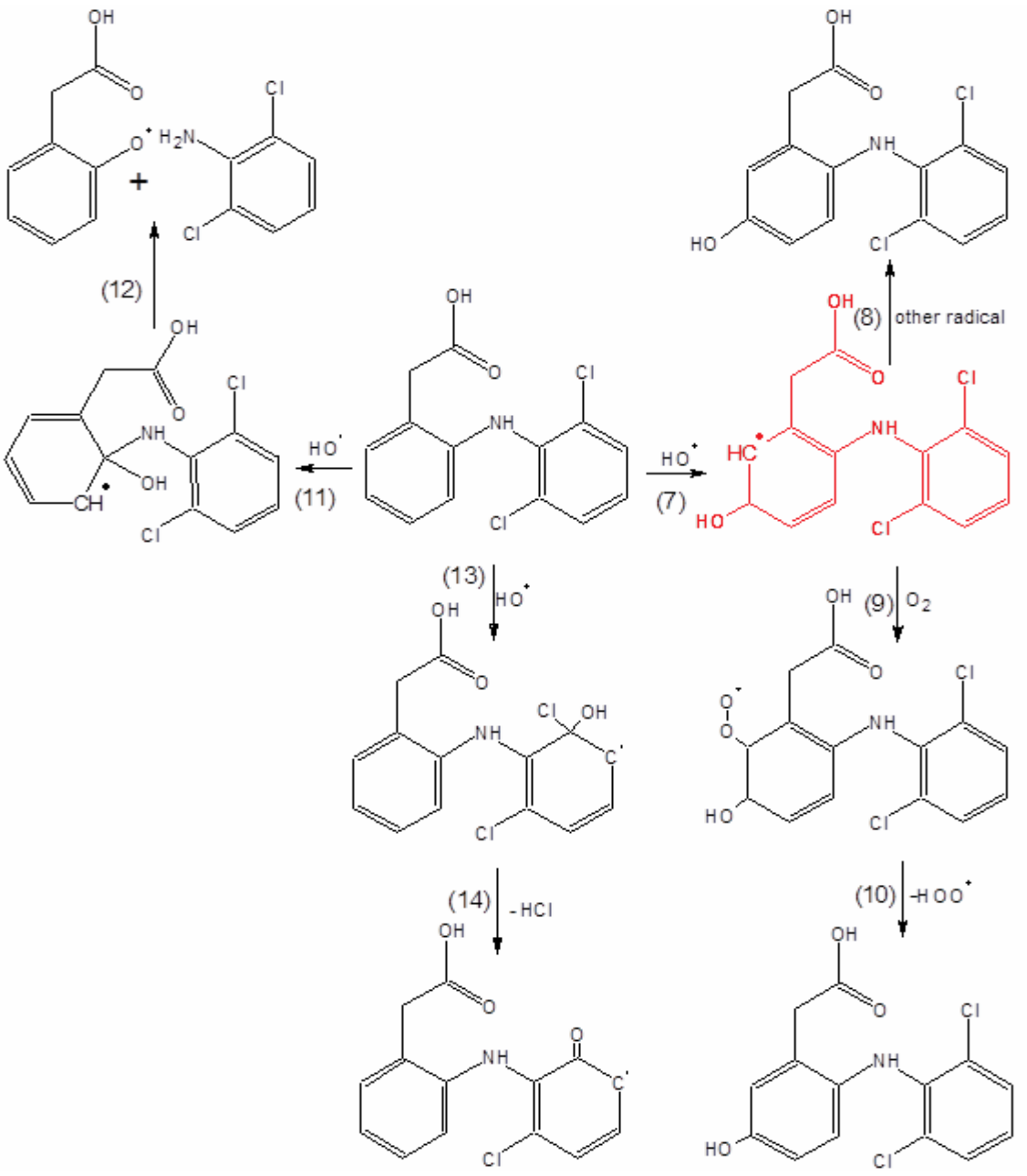


2,6-Dichloroaniline degradation

Anilino Radical



Diclofenac degradation



No anilino or phenoxyl radical

Summary of degradation efficiency

Hydroxyl radical initiated oxidation maleic acid, fumaric acid and phenols proceeds with high efficiency, the one-electron oxidant •OH induces two- to four-electron oxidations. When amino, acetamide or hydrazo groups are attached to the ring the rate is lower, one •OH induces only one–two electron oxidations. The low rate is due to intermediate radicals which have low reactivity with oxygen (penoxyl, anilino, semi-iminoquinone, hydrazyl).

Contribution of reductive radicals (e_{aq}^- and $H^\bullet$) to the oxidative degradation in aerated solution

There is a competition between the reaction with O_2 and the solute

$e_{aq}^{-\bullet} + O_2 \rightarrow O_2^{-\bullet}$	$k_1 = 1.9 \times 10^{10}$ mol^{-1} dm^3 s^{-1}
$H^\bullet + O_2 \rightarrow HO_2^\bullet$	$k_2 = 2.1 \times 10^{10}$ mol^{-1} dm^3 s^{-1}
$HO_2^\bullet \rightleftarrows O_2^{-\bullet} + H^+$	$pK = 4.8 \pm 0.1$

$e_{aq}^{-\bullet} + S \rightarrow S^{-\bullet}$	k_3
$H^\bullet + S \rightarrow HS^\bullet$	k_4

The scavenging capacities (concentration multiplied by of the rate coefficient) determine the main reaction partner

Contribution of H• to the oxidative degradation in aerated solution

In the case of H• reactions $k_2\,[O_2] \le k_4\,[S]$

H• reacts with aromatic molecules in radical addition:

k_4 (Phenol + H•) = 1.9×10^9 $\quad$ $mol^{-1}\ dm^3\ s^{-1}$

$$H^\bullet + C_6H_5OH \longrightarrow {}^\bullet C_6H_6OH \xrightarrow{+O_2} {}^\bullet OOC_6H_6OH$$

$$H^\bullet + HOOCCH{=}CHCOOH \longrightarrow HOOCCH_2\text{-}{}^\bullet CHCOOH$$

$$+ O_2 \longrightarrow HOOCCH_2\text{-}({}^\bullet OO)CHCOOH$$

Contribution of $e_{aq}^{-\bullet}$ to the oxidative degradation in aerated solution

There is a competition between the reaction with O_2 and the solute $e_{aq}^{-\bullet}$ adds to electron deficient parts of molecules, the anion often undergoes fast protonation:

$$e_{aq}^{-\bullet} + HOOCCH{=}CHCOOH \longrightarrow HOOCCH{=}CH^{\bullet}CO^{-}OH \xrightarrow{H^+} HOOCCH_2\text{-}^{\bullet}CHCOOH \xrightarrow{+O_2} HOOCCH_2\text{-}(^{\bullet}OO)CHCOOH$$

$$e_{aq}^{-\bullet} + ClC_6H_4OH \xrightarrow{-Cl^-} {}^{\bullet}C_6H_4OH \xrightarrow{+O_2} {}^{\bullet}OOC_6H_4OH$$

Contribution of $e_{aq}^{-\bullet}$ recations to the oxidative degradation in aerated solution

When $k_1\,[O_2] \le k_3\,[S]$, $e_{aq}^{-\bullet}$ reacts with O_2

Both the self-termination and reactions with S are slow. In self-termination H_2O_2 forms, it may contribute to oxidation, e.g. by reacting with $e_{aq}^{-\bullet}$ and forming $^{\bullet}OH$.

$$2\,HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \quad k = 8 \times 10^5\ mol^{-1}\ dm^3\ s^{-1}$$

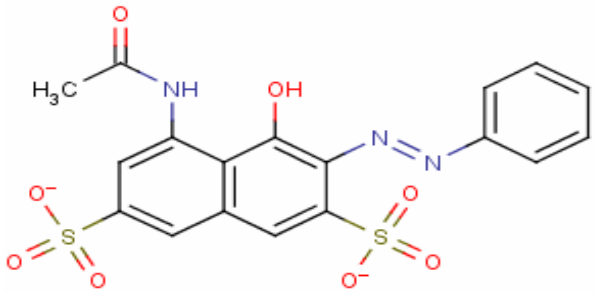
$$HO_2^{\bullet} + O_2^{-\bullet} + H_2O \longrightarrow H_2O_2 + O_2 + OH^-$$
$$k = 9 \times 10^7\ mol^{-1}\ dm^3\ s^{-1}$$

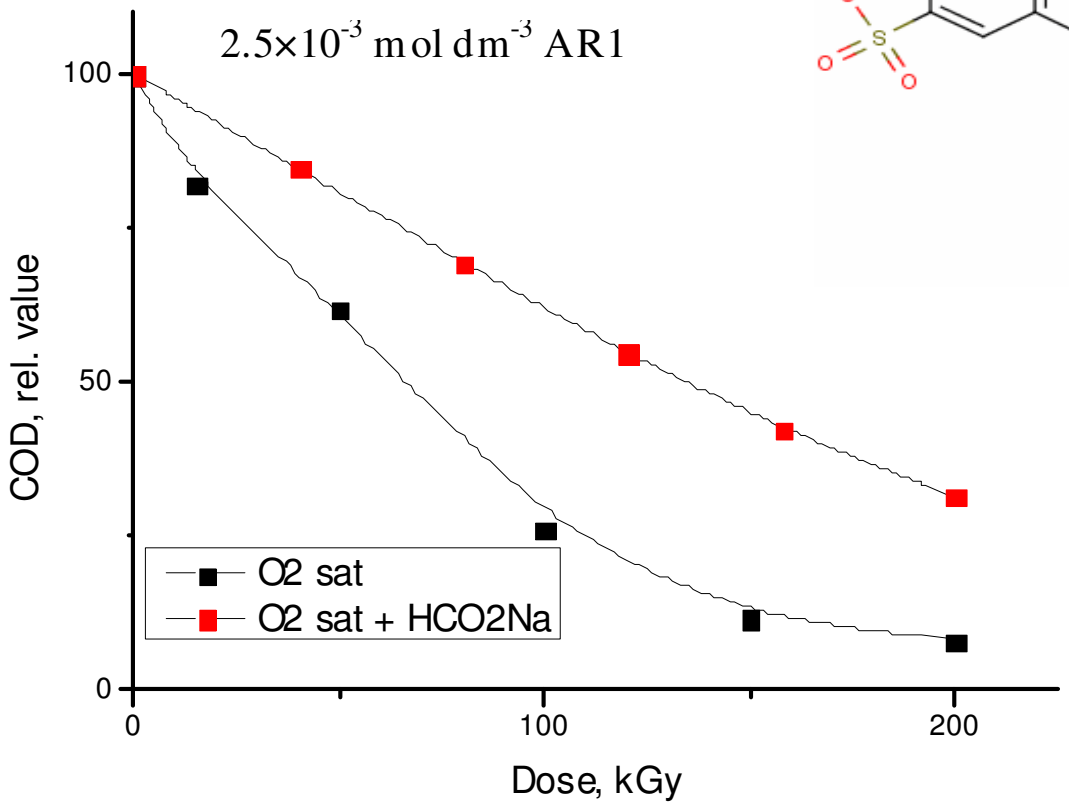
$$e_{aq}^{-\bullet} + H_2O_2 \longrightarrow {}^{\bullet}OH + OH^-$$
$$k = 1.1 \times 10^{10}\ mol^{-1}\ dm^3\ s^{-1}$$

Contribution of $O_2^{-\bullet}/HO_2^{\bullet}$ pair to the oxidative degradation in aerated solution

$$^{\bullet}OH + HCO_2^- \longrightarrow H_2O + CO_2^{-\bullet}$$

$$CO_2^{-\bullet}\ O_2 \longrightarrow CO_2 + O_2^{-\bullet}$$





Contribution of $O_2^{-\bullet}/HO_2^{\bullet}$ pair to the oxidative degradation in aerated solution

$O_2^{-\bullet}/HO_2^{\bullet}$ pair is non-reactive in reactions with aromatics. Little information on the reaction rates. The rate coefficient of the phenol + $HO_2^{\bullet}$ reaction is 5.8×10^2 mol^{-1} dm^3 s^{-1}.

$$HO_2^{\bullet} + C_6H_5OH \longrightarrow {}^{\bullet}HO_2C_6H_5OH \xrightarrow{+\,O_2} \text{products}$$

Similar reactions may also contribute to the degradation of other aromatics.

The reductive radicals, $e_{aq}^{-\bullet}$ and $H^{\bullet}$ in oxygenated solution also contribute to the oxidative degradation


Thank you for your attention