Radiation Processing

Chemical Effects

Reactions of Hydrated Electron

Major Reactions of e^-_{aq}

1. $e^-_{aq} + N_2O \longrightarrow N_2 + O \xrightarrow{H_2O} \cdot OH$

   Used to detect/estimate e^-_{aq} and to increase ·OH yield

2. $e^-_{aq} + O_2 \longrightarrow O_2^{-}\cdot \rightleftharpoons HO_2\cdot$

   Used to produce $O_2^{-}\cdot$, prevalent in systems open to air

3. $e^-_{aq} + C_6H_5I \longrightarrow \cdot C_6H_5I + I^-$

   Dissociative electron capture by halogenated organics can be used to detect and estimate e^-_{aq}

4. $e^-_{aq} + Fe^{3+} \longrightarrow Fe^{2+}$

   $e^-_{aq} + NO_3^- \longrightarrow \cdot NO_3^{2-}$

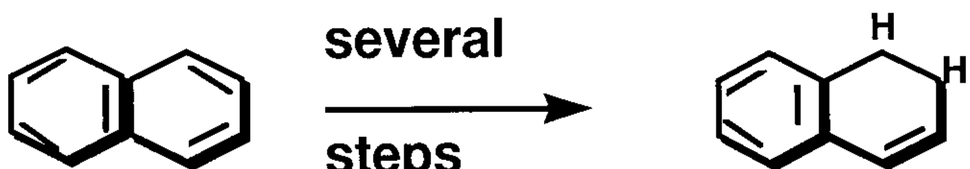
   Reactions with cations and many anions are known to occur

Reactions of Hydrated Electrons (contd)

5. Reduces carbonyls to hydroxy derivatives

$$e^-_{aq} + (CH_3)_2CO \xrightarrow[\text{steps}]{\text{several}} (CH_3)_2\,CHOH$$

6. Decreases aromaticity



Naphthalene — Dihydronaphthalene

7. Reacts with cellular constituents (e.g. amino acids)

$$e^-_{aq} + NH_3^+CHRCOO^- \longrightarrow NH_3 + \cdot CHRCOO$$
$$\longrightarrow \cdot NH_2 + RCHCOOH$$
$$\longrightarrow \cdot H + NH_2CHRCOO^-$$

Reactions of ·OH

The major types of reactions are

1. Addition to double bonds

$$>C{=}C< + \cdot OH \longrightarrow >\underset{}{\overset{OH}{\overset{|}{C}}} - \dot{C}<$$

2. Hydrogen abstraction

$$RH + \cdot OH \longrightarrow R\cdot + H_2O$$

3. Electron transfer

$$Br^- + \cdot OH \longrightarrow \cdot Br + OH^-$$
$$Fe^{2+} + \cdot OH \longrightarrow Fe^{3+} + OH^-$$

Reactions of ·OH (contd)

4. Produce ketones from alcohols

$$(CH_3)_2CHOH + \cdot OH \rightarrow (CH_3)_2\dot{C}OH + H_2O$$

$$(CH_3)_2\dot{C}OH + (CH_3)_2\dot{C}OH \rightarrow \begin{array}{r}(CH_3)_2\text{-}C\text{-}OH\\ |\;\;\;\;\;\;\\ (CH_3)_2\text{-}C\text{-}OH\end{array}$$

$$\rightarrow (CH_3)_2CHOH + (CH_3)_2CO$$

- Hydroxyl radical is just about the most reactive free radical known

Reactions of Hydrogen Atom

The two main reactions are addition to double bonds and hydrogen abstraction

1. Addition to double bond

$$> C = C < + H\cdot \longrightarrow\ > \overset{\displaystyle H}{\overset{|}{C}} - \dot{C} <$$

2. Hydrogen abstraction

$$RH + H\cdot \longrightarrow R\cdot + H_2$$

With oxygen, it gives the superoxide anion

$$O_2 + H\cdot \longrightarrow HO^{\cdot}_2 \longrightarrow O_2^{-\cdot} + H^+$$

Differentiation of Reactive Species

One can differentiate between reactions of the different reactive species by choosing appropriate conditions

- In inert atmosphere (e.g., N_2 or vacuum) all three, e^-_{aq}, $\cdot H$ and $\cdot OH$ are present
- In the presence of N_2O the predominant free radical is $\cdot OH$ (90% $\cdot OH$, 10% $\cdot H$)
- In air the reactive species is mainly $\cdot OH$ (~45% + rather unreactive $O_2^{-}\cdot/HO\cdot_2$ ~55%)
- In the presence of O_2 and formate (10^{-2} to 10^{-1} mol•dm^{-3}) only $O_2^{-}\cdot/HO^{\cdot}_2$ are present

$$\cdot OH + HCO^-_2 \longrightarrow CO^-_2\cdot + H_2O$$
$$\cdot H + HCO^-_2 \longrightarrow CO^-_2\cdot + H_2$$
$$O_2 + CO^-_2\cdot \longrightarrow O^-_2\cdot + CO_2$$

Comparison of ·H With ·OH and e^-_{aq} Reactivity

Inactivation Efficiencies of Reactive Free Radical Species with Ribosomes

Species	Relative Inactivation Efficiency	
	In Vacuum	Expected in air
·OH	1.0	~2.5[a]
e^-_{aq}	0.8	~0.1[b]
·H	4.2	~0.1[b]

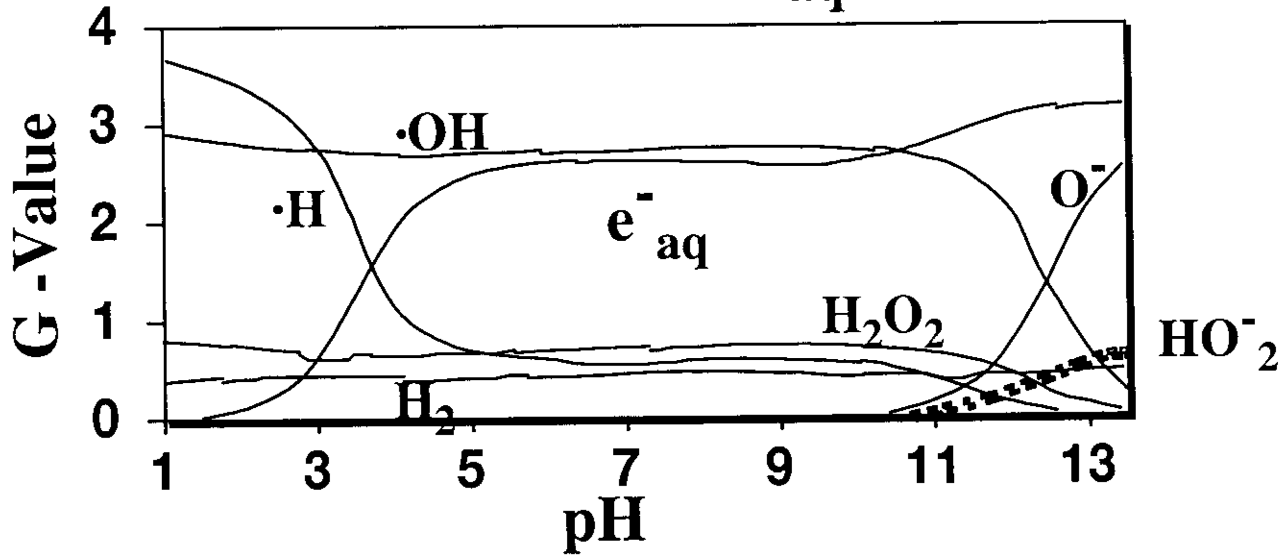
[a] Increased damage due to peroxidation

[b] Damage from superoxide anion (O^-_2•)

Singh and Singh (1983)

pH Dependence of Yields on Radiolysis of Water

$$e^-_{aq} + H^+ \rightarrow \cdot H$$
$$\cdot H + OH^- \rightarrow e^-_{aq}$$



- The pH range of most foods lies between 2 and 8

Some Reaction Rate Constants in Aqueous Solutions at 20°C

Reactant, S	$k(e^-_{aq} + S)$	$K(\cdot OH + S)$	$k(\cdot H + S)$
Fe^{2+}	1.2×10^8	3×10^8	1.6×10^7
Mn^{2+}	6.0×10^7	3×10^8	3×10^7
Cu^{2+}	3.0×10^{10}	3.5×10^8	4.2×10^7
NO^-_2	4.6×10^9	8×10^9	9×10^6
NO^-_3	1.1×10^{10}	slow	5×10^6
$H_2PO^-_4$	4.2×10^6	$<10^7$	no reaction
HCO^-_3	$<10^6$	1×10^7	$\sim 10^4$
CO_2	7.7×10^9	no rection	$\sim 10^4$
Br^-	no reaction	1.1×10^9	no reaction
Cl^-	no reaction	10^9	no reaction
H_2O_2	1.2×10^{10}	2.2×10^7	6×10^7
O_2	2.2×10^{10}	no reaction	2×10^{10}

(Units: $mol^{-1} \bullet dm^3 \bullet s^{-1}$)

In general

- e^-_{aq} is a very strong reducing agent
- $\cdot$H is a weaker reducing agent, and
- $\cdot$OH is a strong oxidizing agent

Some Reaction Rate Constants in Aqueous Solutions at 20°C

Reactant, S	$k(e^-_{aq} + S)$	$K(\cdot OH + S)$	$k(\cdot H + S)$
Fe^{2+}	1.2×10^8	3×10^8	1.6×10^7
Mn^{2+}	6.0×10^7	3×10^8	3×10^7
Cu^{2+}	3.0×10^{10}	3.5×10^8	4.2×10^7
NO^-_2	4.6×10^9	8×10^9	9×10^6
NO^-_3	1.1×10^{10}	slow	5×10^6
$H_2PO^-_4$	4.2×10^6	$<10^7$	no reaction
HCO^-_3	$<10^6$	1×10^7	$\sim 10^4$
CO_2	7.7×10^9	no rection	$\sim 10^4$
Br^-	no reaction	1.1×10^9	no reaction
Cl^-	no reaction	10^9	no reaction
H_2O_2	1.2×10^{10}	2.2×10^7	6×10^7
O_2	2.2×10^{10}	no reaction	2×10^{10}

(Units: $mol^{-1} \cdot dm^3 \cdot s^{-1}$)

In general

- e^-_{aq} is a very strong reducing agent
- $\cdot H$ is a weaker reducing agent, and
- $\cdot OH$ is a strong oxidizing agent

Some Reaction Rate Constants in Aqueous Solutions at 20°C (contd)

Reactant, S	$k(e^-_{aq} + S)$	$K(^{\bullet}OH + S)$	$k(^{\bullet}H + S)$
Aliphatic hydrocarbons	Negligible	10^5 - 10^8 [a]	10^5 - 10^8 [a]
$(CH_3)_2CO$	5.9×10^9	9.0×10^7	3.4×10^5
>C=C<	10^6	$\sim10^9$	$\sim10^9$
>C=C-C=C<	8×10^9	10^{10}	10^9-10^{10}
ROOH, ROOR	10^9-10^{10}	10^5-10^8	10^5-10^8
RCl	10^8-10^9	[b]	[b]
RNO_2	10^9-10^{10}	[b]	[b]
Aromatics	10^7	10^9	$\sim10^8$
-SH	$\sim10^{10}$	$\sim10^{10}$	$\sim10^9$
-SS-	$\sim10^{10}$	$\sim10^{10}$	$\sim10^9$
H_2NCH_2COOH	8.2×10^6	1.6×10^7	7×10^4

[a] Depends on the C-H bond strength, [b] Depends on R

Some Reaction Rate Constants in Aqueous Solutions at 20°C (contd)

- Protection of biological systems by the -SH compounds is due to their very high reactivity with all of the three primary species from water
- The >C=C-C=C< would be the next best. However, its secondary radical could be damaging to biological systems, but RS· is not

Reactions of H_2O_2

1. Formation

$$\cdot OH + \cdot OH \longrightarrow H_2O_2 \text{ (in vacuum/}N_2\text{)}$$
$$O_2^{-}\cdot + O_2^{-}\cdot + 2H^{+} \longrightarrow H_2O \text{ (in air)}$$

2. Reactions

Fenton Reaction $H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + OH^{-} + \cdot OH$

HRP Reaction

$$H_2O_2 + HRP \longrightarrow HRP\text{-}I$$
$$RH + HRP\text{-}I \longrightarrow R\cdot + HRP\text{-}II$$
$$RH + HRP\text{-}II \longrightarrow R\cdot + HRP$$

- Overall, it is a mild oxidizing agent; it oxidizes phenols and inactivates enzymes

Other Secondary Reactive Species

1. Superoxide Anion ($O_2^{-}\cdot$)

- *Formation*

$$e^-_{aq} + O_2 \longrightarrow O_2^{-}\cdot$$

- *Reactions*

$$O_2^{-}\cdot + O_2^{-}\cdot + 2H^+ \longrightarrow H_2O_2 + O_2$$

$$O_2^{-}\cdot + \text{SOD-Cu}^{2+} \longrightarrow \text{SOD-Cu}^{+} + O_2$$

Superoxide Dismutase

$$\text{SOD-Cu}^{+} + O_2^{-}\cdot + 2H^+ \longrightarrow \text{SOD-Cu}^{2+} + H_2O_2$$

2. Singlet Oxygen ($^1O_2$)

- A minor species which oxidizes unsaturated compounds

$$\text{Lipids} + {}^1O_2 \longrightarrow \text{Lipid Hydroperoxide (ROOH)}$$

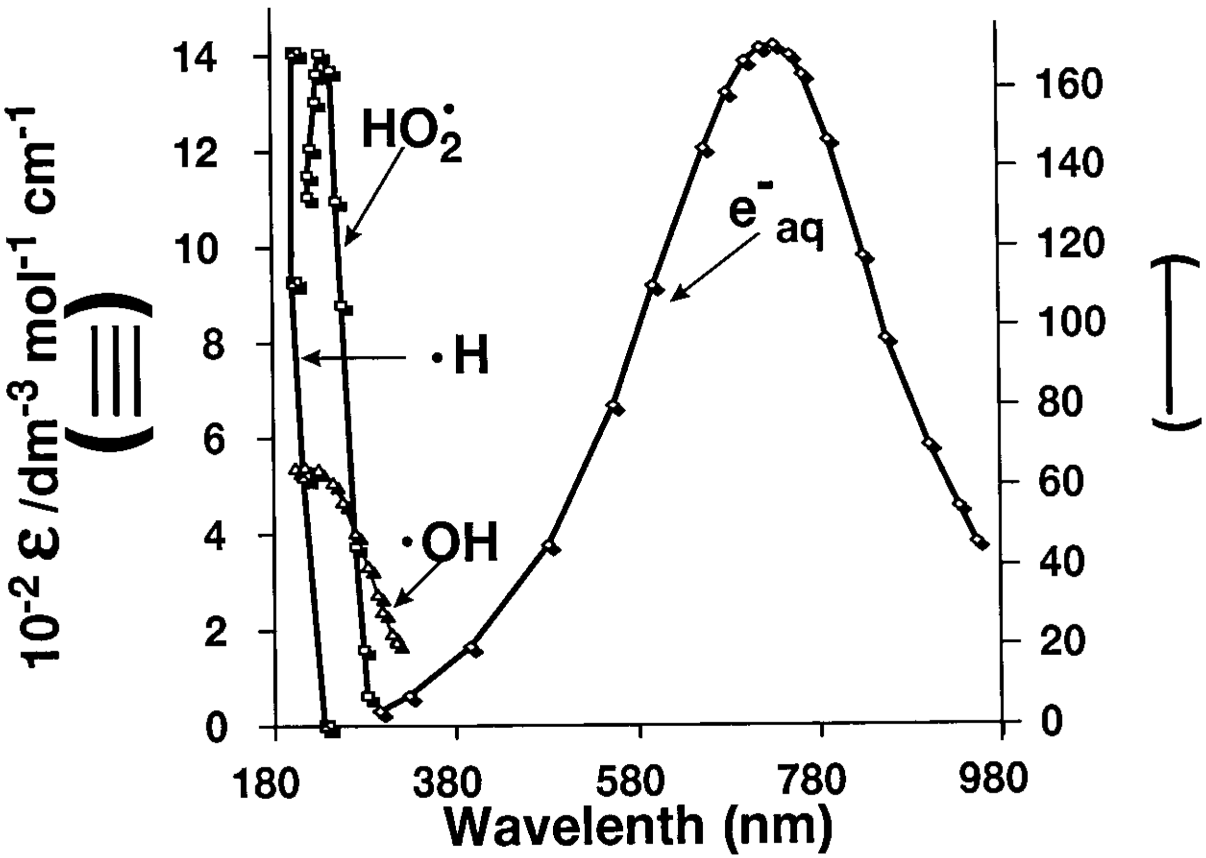
$$\text{ROOH} + Fe^{2+} \longrightarrow RO\cdot + OH^- + Fe^{3+}$$

Alkoxy Radical (Fenton like reaction)

Detection of Various Reactive Species

e^{-}_{aq}	$\cdot OH$	$\cdot H$	H_2O_2
- ESR	-ESR	-ESR	-ESR/Fenton Reaction ($\cdot OH$ formation)
-Optical absorption	-C_2H_4 formation with methional	-Formation of characteristic products following its reactions (e.g., H_2)	-Inhibition of its reaction by catalase
-Reaction with N_2O	-Bleaching of p-nitroso-dimethylaniline -Hydroxylation of phenol and/or salicylic acid -Reaction with tryptophan		-Iodine liberation from acidified KI solutions

Absorption Spectra of Some Species in Water



Reactions of Organic Free Radicals

1. Peroxy Radicals
   - *Formation*

     $R\cdot + O_2 \longrightarrow RO_2\cdot$ (Peroxy Radical)

   - *Reactions*

     $RO_2\cdot + RSH \longrightarrow ROOH + RS\cdot$

     (hydroperoxide) (thiyl radical)

     $RO_2\cdot + RO_2\cdot \longrightarrow 2\,RO\cdot + O_2$

     (alkoxy radical)

     $\longrightarrow 2\,RO\cdot + {}^1O_2$

     $RO\cdot + RO\cdot \longrightarrow RO - OR$

     (organic peroxide)

   - Peroxy radicals are the main vehicle of lipid peroxidation leading to rancidity of oils and fats

Reactions of Organic Free Radicals (contd)

2. Hydrogen Abstraction

$$R\cdot + R^1H \longrightarrow RH + \cdot R^1$$

(less efficient than $\cdot OH$ or $\cdot H$)

3. Addition to Double Bonds

$$R\cdot + {>}C=C \longrightarrow {>}\overset{\overset{R}{|}}{C}-\dot{C}{<}$$

(usually, not as efficient as the addition of $H\cdot$ or $\cdot OH$)

4. Recombination

$$R\cdot + R\cdot \longrightarrow R\text{-}R$$

5. Disproportionation

$$RCH_2\dot{C}H_2 + RCH_2\dot{C}H_2 \longrightarrow RCH_2CH_3 + RCH=CH_2$$

Radiolysis of Cyclohexane

C_6H_{12}

Products	Initial Yield (molecules/100 eV)
H_2	5.6 ± 0.1
$c\text{-}C_6H_{10}$	3.2 ± 0.2
$(c\text{-}C_6H_{11})_2$	1.76 ± 0.05
$CH{=}CH(CH_2)_3CH_2$	0.40 ± 0.05
$c\text{-}C_5H_7\text{-}CH_3$	0.15 ± 0.01
$c\text{-}C_6H_{11}\text{-}(CH_2)_4CH{=}CH_2$	0.12 ± 0.02
$n\text{-}C_6H_{14}$	0.08 ± 0.02
unidentified C12	~ 0.05
$c\text{-}C_6H_{11}\text{-}C_2H_5$	~ 0.04

Gamma Radiolysis of Liquid Cyclohexane in the Presence of Oxygen

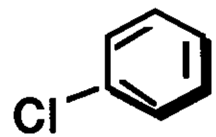
Product	G (Product)	
	Evacuated Sample	Sample in O_2 (2 mol m^{-3})
1-Hexene	0.5	0.26
Hexane	0.1	<0.01
Methylcylopentane	0.3	~0.03
Cyclohexene	3.2	1.5
Bicylohexyl	1.9	0.29
Cylohexanol	0	3.2
Cylohexanone	0	2.6
Peroxides	0	0.61

Radiolysis of Benzene

 C_6H_6

Products	G (molecules/100 eV)
Hydrogen	0.039
Ethylene	0.022
Acetylene	0.020
1,4-Cyclohexadiene	0.021
1,3-Cyclohexadiene	0.008
Phenyl-2,4-Cyclohexadiene	0.021
Phenyl-2,5-Cyclohexadiene	0.045
Biphenyl	0.065
C_6 units incorporated in polymers	0.8

Radiolysis of Chlorobenzene Yields of Major Products[a]



C_6H_5Cl

Product	G(Product)
Hydrogen	0.01
Hydrochloric acid	0.25
Benzene	2.91
Biphenyl	0.12
Dichlorobenzene	0.36
Chloro-biphenyl	0.90

[a] Dose, 208/kGy (Spinks and Woods, 1990)

γ- Radiolysis of Liquid Acetone and Methyl Acetate at ~ 22-28°C, G(Products)

Product	Acetone (CH_3COCH_3)	Methyl Acetate (CH_3COOCH_3)
Hydrogen	0.50	0.76
Carbon Monoxide	0.73	1.64
Carbon Dioxide	-	0.96
Methane	1.74	2.03
Ethane	0.24	0.34
Acetaldehyde	0.09	-
Dimethyl Ether	-	0.15
Acetic Acid	0.31	-
Biacetyl	0.28	-
Methyl Ethyl Ketone	0.18	-
2-Propanol	0.09	-
$(CH_3COCH_2)_2$	0.27	-
$CH_3COCH_2COCH_3$	0.11	-

Conclusions

- Understanding of the detailed chemical processes occurring on irradiation has helped develop many of the commercial applications of radiation processing, e.g., curing of coatings, crosslinking of polyethylene, and purification of water in the presence of ozone

- Continuing effort in this area is needed to improve current, and develop new, chemical effect based processes