Concepts and definisions

- Radiation chemistry: the effect of radiation (usually ionising) on chemical compounds
- Hot-atom-chemistry: the effect of radioactive transformations or nuclear reactions on chemical compounds

Books:
Spinks and Woods: An introduction to radiation chemistry (1991)

Farhataziz and Rodgers: Radiation Chemistry (1987)

Concepts and definisions

- Average energy for formation of an ion pair (W) (not the same as ionisation energy)
- G-value (G(X)) -“radiation chemical yield”
  - G(X) is a measurement of the probability of formation of the product X in a given radiation chemical reaction
  - G(X) number of units of X formed per. 100 eV absorbed radiation energy
  - G(-Y) number of units of irradiated compound converted per 100 eV radiation energy
  - $G = (M/N)(100/W)$
    - M - number of species formed
    - N - number of original species consumed
    - W - number of eV per ion- or radical pair
- $1 < G < 5$ Simple reactions
- $10 < G < 25$ High values
- $G \sim 10^5$ Extreme values (catalytic effects)

Radiation chemistry in gases

Gas	H_2	He	Xe	NH_3	CH_4	Air
Ionisation energy (eV)	15.6	24.5	12.1	10.8		
Energy loss pr.ion pair(eV) 5.3 MeVα	36.5	43	22	39	29	35
Energy loss pr.ion pair 3-20 keV e^-	36.3	42	22		27	34
Fraction to ionisation	.43	.58	.55	.28		

Average values for the ion pair energies

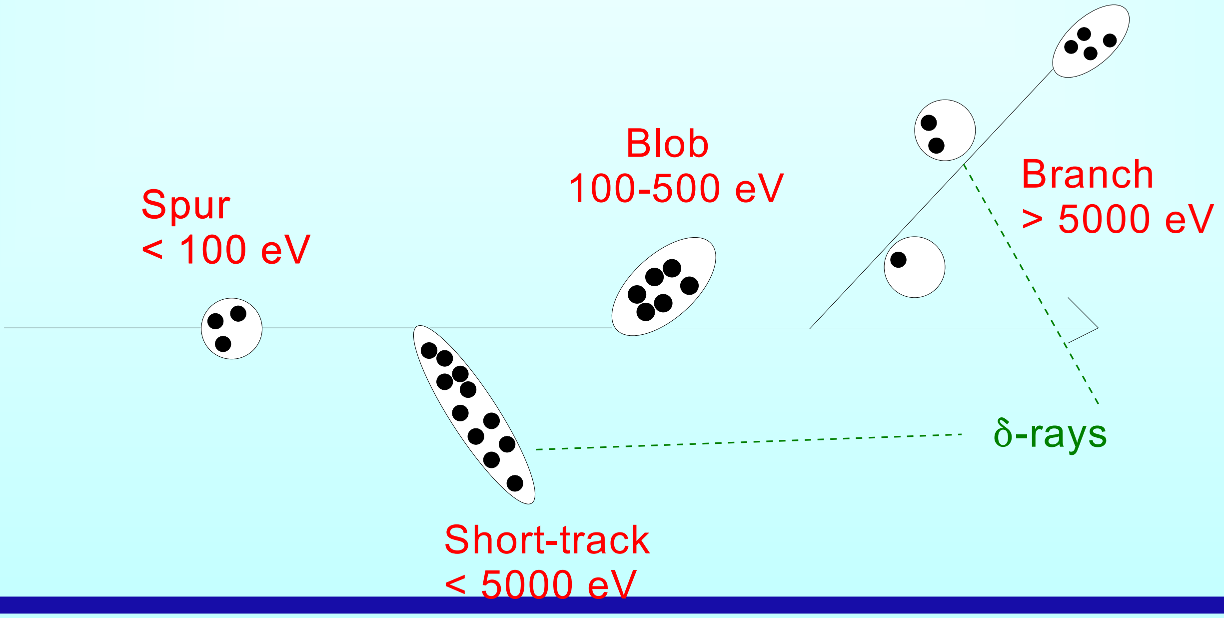
Only a part of the energy needed goes to the ionisation itself. The rest goes to thermal transfer and excitation

"Spurs, blobs and short-tracks"

The number of ion pairs formed within a local region is important.

A high number of ion pairs gives a considerably increased possibility for recombination and formation of particular excited states.

Spur: < 100 eV deposited
Blob: 100 - ~500 eV deposited
Short-track: > ~500 eV deposited



“Spurs, blobs and short-tracks”

In the discussion of the interaction of radiation with matter (Bethe-Bloch) we have used the so-called CSDA - i.e. the continuous slowing down approximation.

Thius approach does not consider the “fine sructure” in the medium slowing down the radiation, nor that biologic material is in effect single molecules

I reality, the interaction is not a continuous process, but a sequence of single events (”spurs”). Each spur gives 2-3 ion pairs which are initially isolated from each other.

“Spurs, blobs and short- tracks”

For low-LET particles each spur develops by itself and initially independent of what happens elsewhere in the matrix

At high-LET radiation and towards the end of each track for low-LET radiation, a large nukber of spurs will overlqap an give a continuous picture -“short-tracks”.

Low energy electrons give rise to “blobs”.

In some cases, single interactions ca give large transfer of energy to one single electron, so-called δ-rays, a name originating from a classical scientific misunderstanding.

Radiation chemical reactions

Primary processes: (10^{-17} - 10^{-16} s)

Ionisation: A ➳ $A^+ + e^-$

Excitation: A ➳ A^*

(➳ = ionising radiation)

Sekundary processes: post-ionisation

$A^+ \rightarrow R^+ + R'$	dissosiation
$A^+ + e^- \rightarrow A^*$	recombination
$A^+ + X \rightarrow A + X^+$	charge transfer
$A^+ + X \rightarrow Y^+$	chemistry

Secondary processes: post-excitation

$A^* \rightarrow A + h\nu$	fluoresence
$A^* \rightarrow R\bullet + R'\bullet$	radical dissosiation
$A^* \rightarrow R^+ + R'^-$	ion dissosiation
$A^* + X \rightarrow Y$	chemistry
$A^* + X \rightarrow A + X + E_{kin}$	heat transfer
$A^* + X \rightarrow A + X$	excitation transfer
$A^* + A \rightarrow A + A^¤$	-----------”---------------

(¤<*)

Secondary processes: 10^{-10} - 10^{-7} s

Radiation chemistry in water

Primary processes: $(10^{-17} - 10^{-16}$ s)

Ionisation: A ➳ $A^+ + e^-$

Excitation: A ➳ A^*

(➳ = ionising radiation)

Originally: two models.

Samuel-Magee:

High recombination:

H_2O ➳ $H_2O^+ + e^-$ followed by

$H_2O^+ + e^- \rightarrow H_2O^{**}$ excited molecule

$H_2O \rightarrow H\bullet + OH\bullet$

Electrons must have short range

Lea-Gray-Platzman

Formation of “solvatised electron”

H_2O ➳ $H_2O^+ + e^-$ followed by e.g.

$H_2O + e^-(aq) \rightarrow OH^- + H\bullet$ (slow reaction)

Electrons must have longer range

Radiation chemistry of water

Radiation chemistry developed largely from the experiences in water vapour, where one has the primary processes:

$H_2O + h\nu \rightarrow H\bullet + OH\bullet$ and
$H_2O + h\nu \rightarrow H_2 + O\bullet$ (weaker)
$H_2O + h\nu \rightarrow H_2O + e^-$ (weaker)

It is also possible to excite the water molecule and the product into different quantum states with different probablility, depending on the wavelength of the electromagnetic radiation.
The conditions in water wapour will of course be quite different from a liquid.

Radiation chemistry of water

Main reactions:

$H_2O \rightsquigarrow H_2O^+ + e^-$

$H_2O \rightsquigarrow H_2O^*$

$H_2O^+ + H_2O \rightarrow H_3O^+ + OH\bullet$

The species H_2O^+ is very reactive and disappears instantaneously from the system, i.e. within 10^{-17} - 10^{-16} s.

In liquid form, all thermal species are hydratised within 10^{-11} s, excitation energy is more rapidly transferred than in gases, and diffusion is much slower than in gases.

Species formed close to each other, will have a large probability to influence each other.

Further important species

$e^-(aq)$ - the solvatised electron - a well defined and well caracterised “chemical compound”, with its own reactions

H• - hydrogen radical

OH• - hydroxyl radical

H_2O_2 - hydrogen peroxide
formed in several ways

HO_2^- - hydroperoxide ion
corresponding base

O_2^{2-} - perokxide ion
corresponding base

O_2^- - superoxide ion
formation: $e^-(aq) + O_2 \rightarrow O_2^-$

$HO_2\bullet$ - hydroperoxyl radical
corresponding acid
formation: $H\bullet + O_2 \rightarrow HO_2\bullet$
or: $O_2^- + H^+ \rightarrow HO_2\bullet$

Further important species

When solutions are irradiated, H_2(g) and O_2(g) are formed, often close to the ratio 2:1. Other gases may also be formed, depending upon the chemical content of the sample

Neutral, non-radical radiation chemical species are assumed to form in radical/radical reactions, e.g.

$H\bullet + H\bullet \rightarrow H_2$ and
$OH\bullet + OH\bullet \rightarrow H_2O_2$
$H\bullet + HO_2\bullet \rightarrow H_2O_2$
etc.

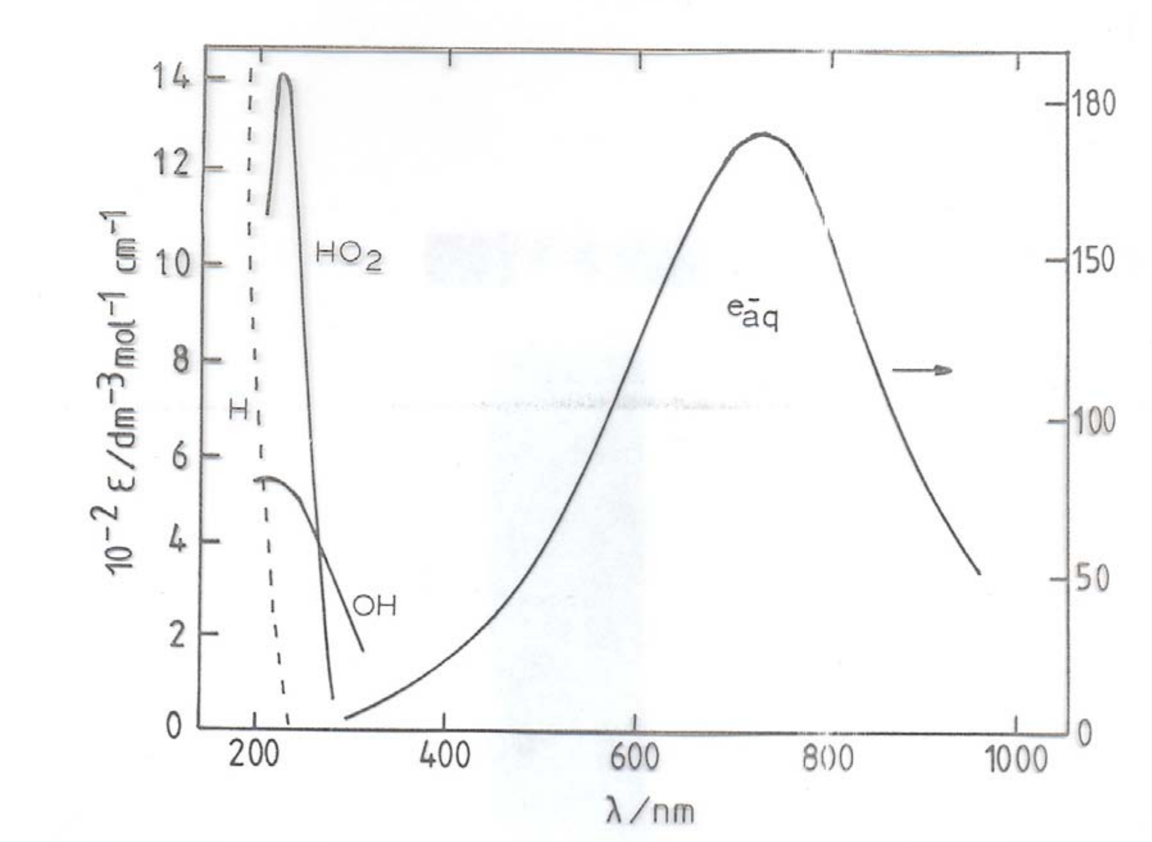
Molecular species are most easily formed where the radical concentration is highest, in “short-tracks “ and “blobs”.

The solvatised electron, $e^-(aq)$

The presence of solvatised electrons in solutions was proposed due to relationships found between reaction rates and PH or ione strength which cound not be explained by acid/base considerations.

The solvatised electron has a characteristic absorption spectrum.
Its half-life is of the order of 200 μs.

The solvatised electron, $e^-(aq)$



The solvatised electron has a characteristic absorption spectrum making it easy to distiguish from other important products

The solvatised electron, e^-(aq)

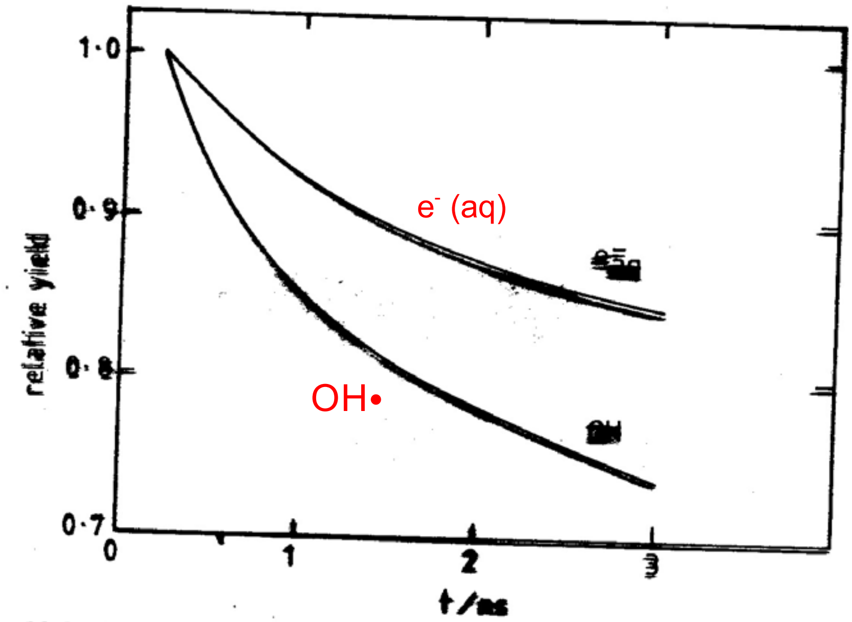


Figure 10-3. Decay of e_{aq}^- and OH produced by a 30-ps pulse of 20-MeV electrons in water. (Reproduced with permission.[39])

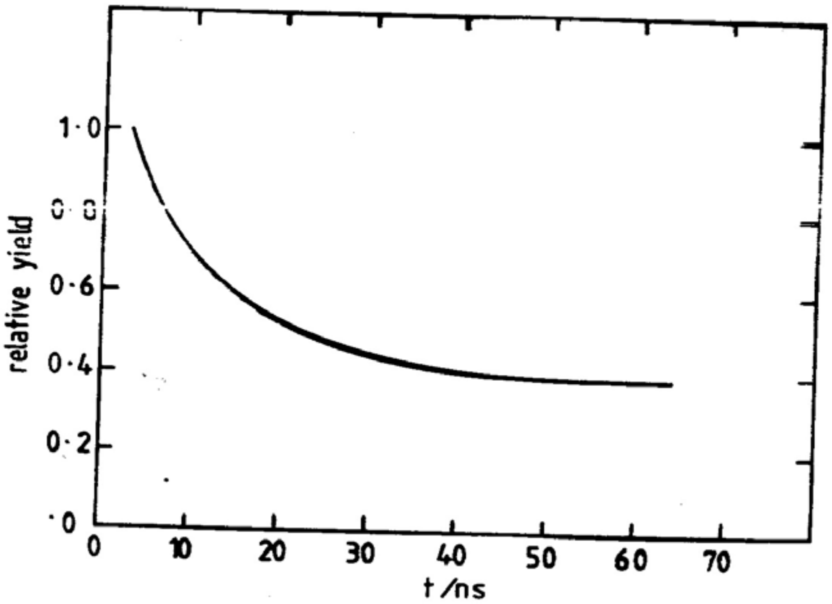


Figure 10-4. Decay of e_{aq}^- produced by a 1-ns pulse of 3-MeV protons in water. (Reproduced with permission.[39])

The solvatised electron, $e^-(aq)$

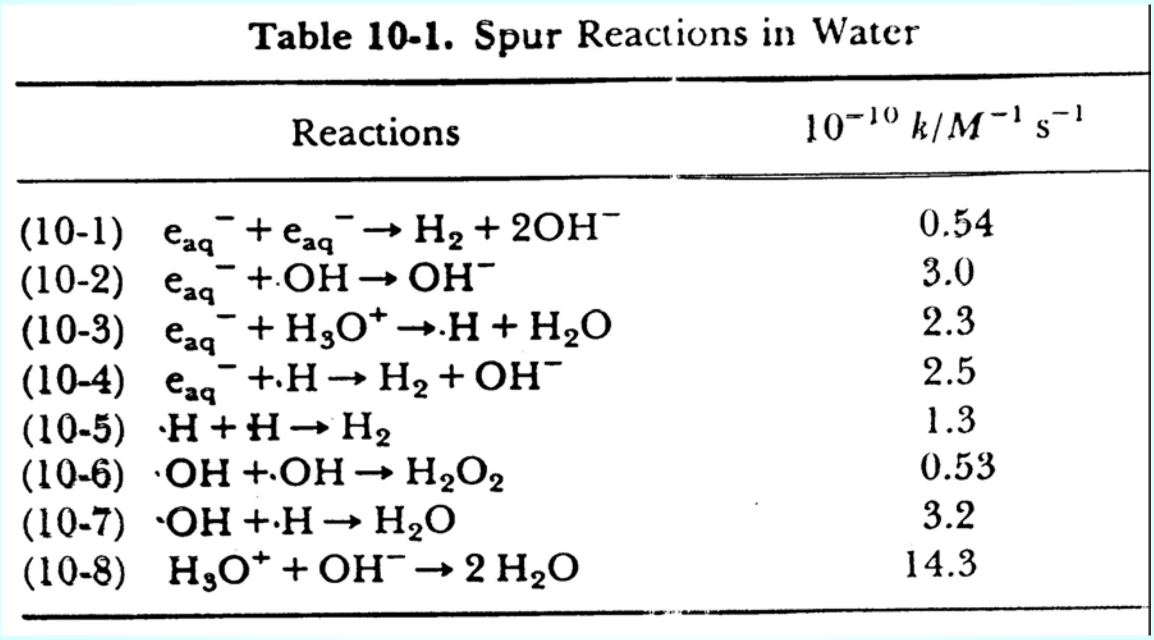


Table 10-1. Spur Reactions in Water

	Reactions	$10^{-10}\,k/M^{-1}\,s^{-1}$
(10-1)	$e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2OH^-$	0.54
(10-2)	$e_{aq}^- + \cdot OH \rightarrow OH^-$	3.0
(10-3)	$e_{aq}^- + H_3O^+ \rightarrow \cdot H + H_2O$	2.3
(10-4)	$e_{aq}^- + \cdot H \rightarrow H_2 + OH^-$	2.5
(10-5)	$\cdot H + \cdot H \rightarrow H_2$	1.3
(10-6)	$\cdot OH + \cdot OH \rightarrow H_2O_2$	0.53
(10-7)	$\cdot OH + \cdot H \rightarrow H_2O$	3.2
(10-8)	$H_3O^+ + OH^- \rightarrow 2\,H_2O$	14.3

Some typical chemical reactions of the solvatised electron

Two main mechanisms

We concentrate in this course the attention to radiation chemistry in:

1) Water
2) Biologically interesting molecules in aqueous medium.

Radiation chemical reactions can be classified as direct or indirect

At indirect reactions, ionisations and excitations from primary radiations leads to formation og radicals and reactive chemical species in a solvent (water). These will in turn react with the biologic material.

By direct reactions, the primary radiation destroys the biologic material itself, the intermediate stadium (radicals) is insignificant or non-existent.

Two main mechanisms (ctd.)

Direct reactions dominate by irradiation with high LET radiation, and the domination is complete at values e.g.
LET ~100 keV/μm
(typical value for an α-particle of 5 MeV)

Indirect reactions dominate by irradiation with low-LET radiation, and the domination is complete at values e.g.
LET ~ 0.2 keV/μm
(typical value for a β-particle of 1 MeV)

For direct mechanism, the chemical conditions are not important. By indirect mechanism, chemistry is very important.

Radical reactions

Radicals formed by irradiation of water in biologic material may react further chemically with more complex biologic molecules:

Typical reactions:

$RH_2 + H\bullet \rightarrow RH\bullet + H_2$(radical formation)

$RH_2 + OH\bullet \rightarrow RH\bullet + H_2O$ (radical form)

$RH\bullet + R'H\bullet \rightarrow RR'H_2$ (radical combination)

$R\bullet + O_2 \rightarrow RO_2\bullet$ (radical-peroxide)

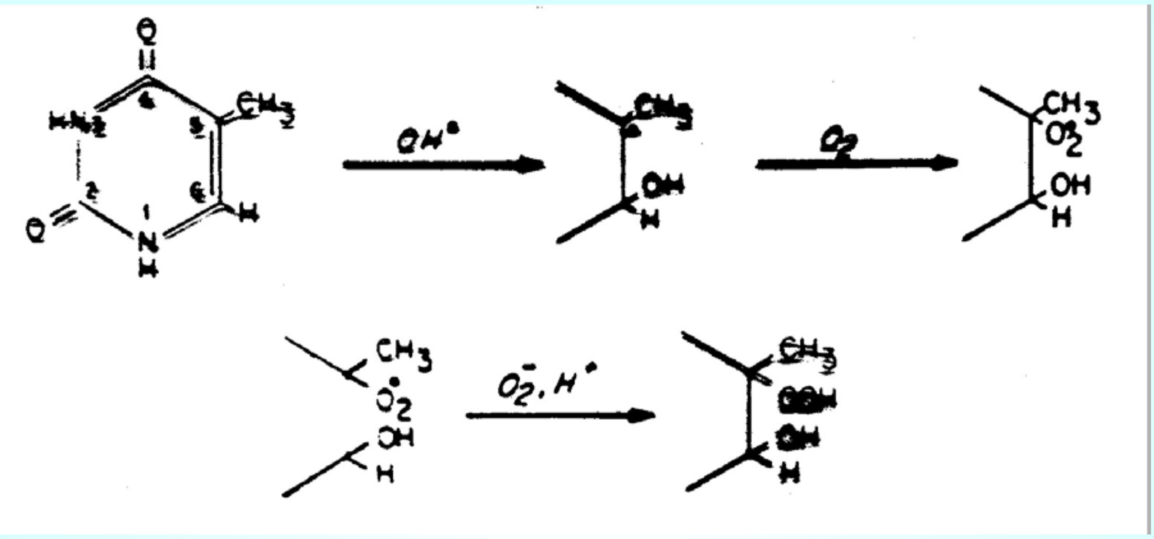
$RO_2\bullet + R'H \rightarrow R'\bullet + ROOH$ (hydroperoxide)

$RO_2\bullet + R'\bullet \rightarrow ROOR'$ (peroxide)

+ others

The presence of oxygen is in order to form peroxides and hydroperoxides, which are very cellularly toxic, and for formation of $HO_2\bullet$. Oxygen increases the degree of radiation damage and functions thus a **“radiosensitizer”**

Radical reactions



A radiation chemical mechanism suggested for thymin (one of the DNA bases)

Radiosensitizers

Radiosensitizers: compounds increasing the effect of ionising radiation on biologic material.

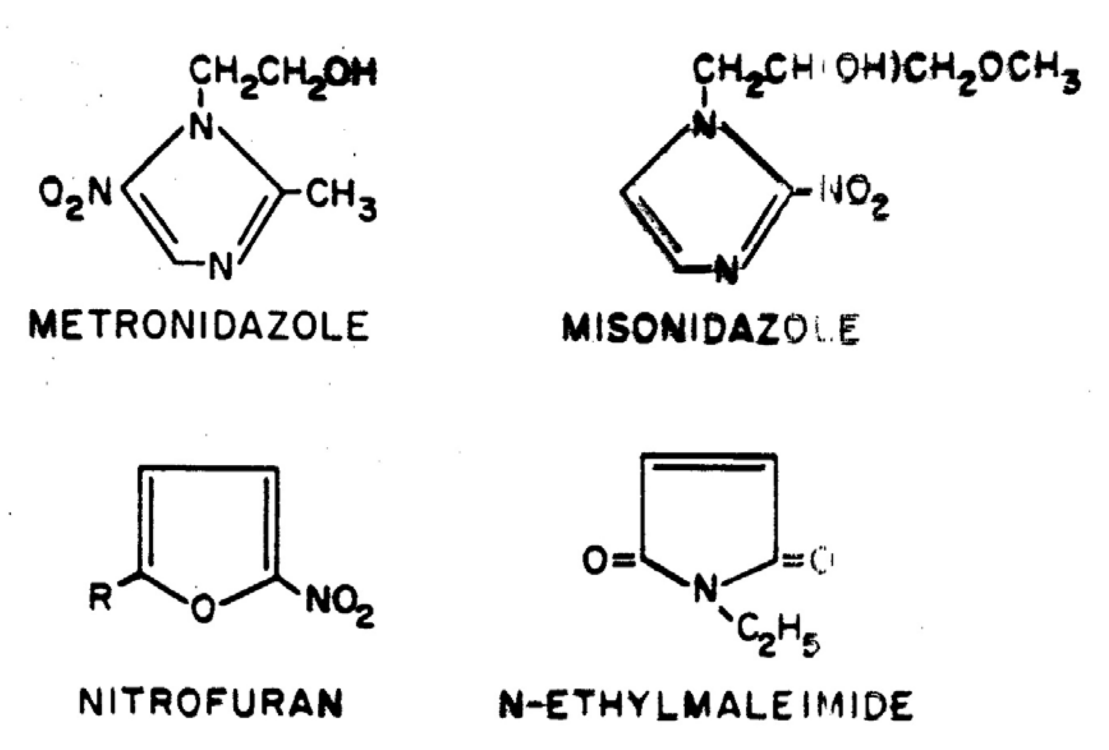
Already mentioned: O_2

Others:

Halogenated pyrimidines:
Can replace “correct” building-blocks in the DNA synthesis and weaken the DNA when incorporated

Nitroimidazoles
Replace oxygen in radical mechanisms by irradiation. These compounds metabolise much slower than oxygen and are therefore able to penetrate better into hypoxic tissue.

Radiosensitizers



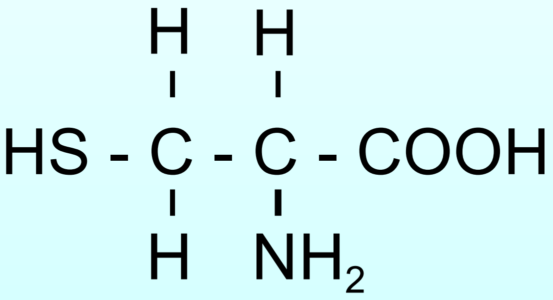
Basic structures for some important radiosensitizers

Radioprotectors

Radioprotectors: Compounds decreasing the effect of ionising radiation on biologic material.

General:
Radioprotectors contain thiol-groups (-SH)

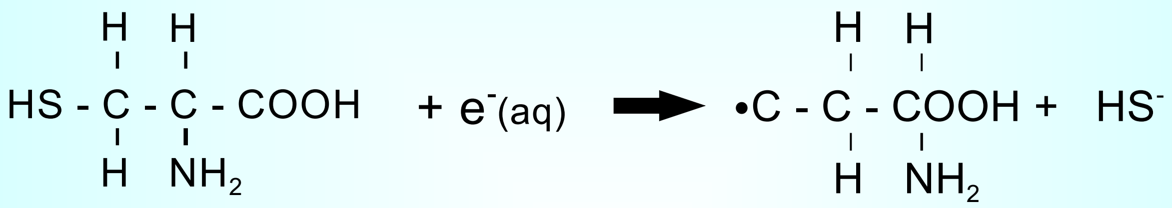
The effect of radioprotectors is to function as radical scavengers, i.e. to react with radicals before they can react with vital molecules.
Ex. Cystein:



$$HS - \underset{H}{\overset{H}{C}} - \underset{NH_2}{\overset{H}{C}} - COOH$$

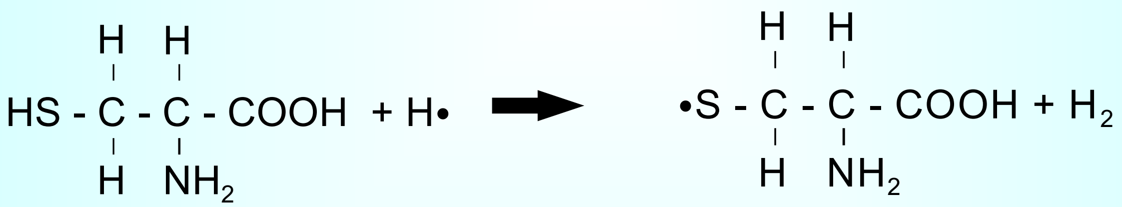
Radioprotectors

Compounds containing SH-groups can react with different radicals in many ways, e.g.



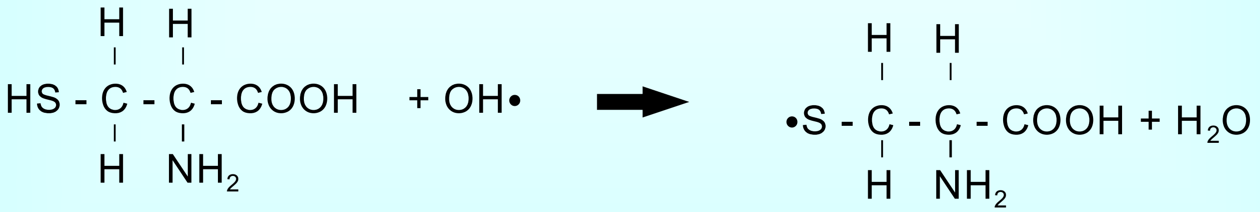
$$HS - \underset{H}{\overset{H}{C}} - \underset{NH_2}{\overset{H}{C}} - COOH + e^{-}(aq) \rightarrow \bullet \underset{H}{\overset{H}{C}} - \underset{NH_2}{\overset{H}{C}} - COOH + HS^{-}$$

or



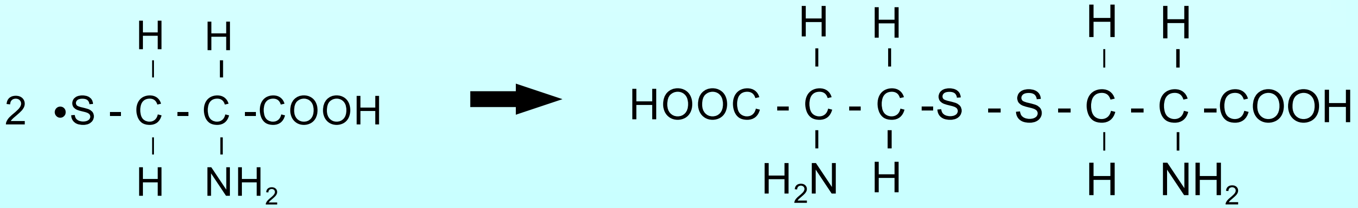
$$HS - \underset{H}{\overset{H}{C}} - \underset{NH_2}{\overset{H}{C}} - COOH + H\bullet \rightarrow \bullet S - \underset{H}{\overset{H}{C}} - \underset{NH_2}{\overset{H}{C}} - COOH + H_2$$

or



$$HS - \underset{H}{\overset{H}{C}} - \underset{NH_2}{\overset{H}{C}} - COOH + OH\bullet \rightarrow \bullet S - \underset{H}{\overset{H}{C}} - \underset{NH_2}{\overset{H}{C}} - COOH + H_2O$$

two can give



$$2\ \bullet S - \underset{H}{\overset{H}{C}} - \underset{NH_2}{\overset{H}{C}} - COOH \rightarrow HOOC - \underset{H_2N}{\overset{H}{C}} - \underset{H}{\overset{H}{C}} - S - S - \underset{H}{\overset{H}{C}} - \underset{NH_2}{\overset{H}{C}} - COOH$$

Cystin

Radiation chemistry and biology

Radiation chemistry has important consequences on radiation biology, radiation biophysics, medical physics, radiology, clinical radio-oncology etc.

The effect on more or less complex systems (from humans to cells in culture) depend not only on the radiation dose, but also on parameters e.g:
Doserate
Repetition frequency
Oxygenation - hypoxia
LET-value.
Cell phase and radiation sensitivity

All this determines the general radiation chemical status of the system

(Much) more details, see
C. von Sonntag: “The chemical basis of radiation biology”