

RADIOLYSIS OF WATER

The human body is more than two-thirds water. Ionizing radiation can break up water molecules into «bits» called free radicals. These highly reactive species cause various chemical modifications to essential cell constituents, in particular DNA.



Emmanuel Joly/CEA

Pulse radiolysis apparatus installed at CEA/Saclay for the study of the chemical properties of free radicals derived from the decomposition of water by ionizing radiation. Here, setting the light beam used to identify the radicals by analysis of their absorption spectra.



Radically reactive species

When water is irradiated by **ionizing radiation** the first step, whatever the nature of the radiation, is ionization. The direct excitation of the water molecules, each composed of two hydrogen atoms H and one oxygen atom O, is a minor process compared with the ionization. During the ionization:



the ejected electron can possess enough energy to go on to ionize further molecules of water. The ionized water molecule bears an unpaired electron denoted by a dot •. This first step, which is a

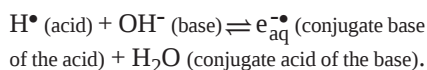
very simple one, since there is no chemical bond cleavage, takes place irrespective of the nature and intensity of the radiation. It is followed by extremely fast secondary reactions that ultimately yield stable molecular products, hydrogen H_2 and hydrogen peroxide H_2O_2 , and free radicals or radical ions $\text{H}^\bullet$, $\bullet\text{OH}$, $\text{HO}_2^\bullet$, and $\text{e}_{\text{aq}}^{\bullet-}$. These are atoms, molecules or ions that bear an electron that is not paired in any chemical bond. They are much more reactive than the molecular products and therefore have a very short lifetime, of the order of a microsecond ($1 \mu\text{s} = 10^{-6} \text{s}$). To identify them in real time a specific technique has to be used: pulse radiolysis (box). Oxygen is

When radioactivity was first discovered researchers soon became interested in the effect on water of the radiation from radium. Before the First World War the French chemist André Louis Debierne (1874 - 1949), who worked in the same laboratory as Pierre and Marie Curie, had already postulated that the radio-induced decomposition of water involved a mechanism in which radicals were implicated. Here, André Louis Debierne in his laboratory in about 1901.



ARCHIVES CURIE AND JOLIO-CURIE

not a primary product of the radiolysis of water. It is formed mainly by the reaction of hydroxyl radicals, $\bullet\text{OH}$, with hydrogen peroxide. The hydrated electron, e_{aq}^- , is not bound to particular water molecules, but is trapped in a cavity made up of neighboring water molecules that form a hydration sphere, analogous to that observed for ions in aqueous solution. The existence of this highly reactive species was postulated as long ago as the twenties but was only identified experimentally forty years later. Chemically, the hydrated electron can be considered as the conjugate base⁽¹⁾ of the $\text{H}^\bullet$ radical, which is thus the simplest possible acid:



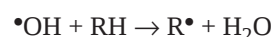
The $\text{H}^\bullet$ radical and the hydrated electron are very powerful reducing agents⁽²⁾ compared with the hydrogen molecule. In parallel, the hydroxyl radical is a potent oxidizing agent⁽²⁾, much more potent than hydrogen peroxide. Biologically, it is the most active of all the

species generated by the radiolysis of water.

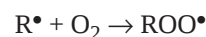
The hydroxyl radical attacks organic molecules by three main mechanisms. It can remove an electron from the molecule. This oxidation process by electron transfer, which causes ionization of the molecule as if it had absorbed the radiation energy directly, is relatively rare. The hydroxyl radical will also remove a hydrogen atom from an organic molecule. This process results in the cleavage of carbon-hydrogen (C—H) bond. It can also add on to a C = C double bond or an aromatic ring⁽³⁾ such as that of benzene or one of its derivatives. All three of these mechanisms yield organic free radicals.

The sensitizing effect of oxygen

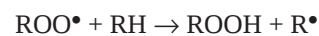
It has long been known that oxygen makes **cells** more vulnerable to radiation. Although the mechanisms involved are many and complex, one of the causes of this radiosensitization is the reaction of organic free radicals with oxygen to form a peroxy radical. If an organic molecule is symbolized by the formula RH, where R represents the organic radical, then the reactions can be written:



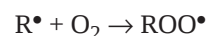
cleavage of a C—H bond



formation of a peroxy radical



formation of an organic peroxide



formation of another peroxy radical.

(1) An acid is converted into its conjugate base by losing a proton (H^+ ion). A base is converted into its conjugate acid by gaining a proton.

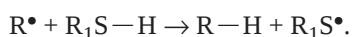
(2) A reducing agent is a substance that will release electrons readily; an oxidizing agent is a substance that will capture electrons readily.

(3) An aromatic ring is a feature of an organic compound in which double bond-forming electrons are delocalized in a ring, usually made up of carbon atoms, giving it high stability.

This sequence of chemical reactions amplifies the initial damage caused by the hydroxyl radical.

Radioprotective compounds

Conversely, a certain amount of chemical damage can be repaired before the process becomes irreversible. Thus a C—H bond, the cleavage of which yields a free radical, can be restored by adding a substance that readily gives up a hydrogen atom. These substances include for instance organic compounds containing an S—H bond, such as thiols, which are alcohol analogs in which oxygen is replaced by sulfur, S:



The $R_1S\cdot$ radical is weakly reactive and unlike the peroxy radical is unable to remove an atom of hydrogen from another organic compound. Other compounds, in the quinone family⁽⁴⁾, act by electron transfer.

The paradox of the decomposition of water

Water undergoes a specific self-repair process that long puzzled scientists. When very pure water is irradiated with X- or gamma rays it apparently does not decompose, and no formation of hydrogen or hydrogen peroxide is experimentally detected. In contrast, in the presence of air or chemical substances decomposition is observed. On the other hand water is always decomposed by alpha particle irradiation. In 1958 an American team led by Augustine O. Allen solved this paradox by showing that hydrogen and hydrogen peroxide generated by irradiation recombined in a chemical chain reaction involving $H\cdot$ and hydroxyl radicals. This reaction is inhibited in the presence of oxygen or solutes in the water. Irradiation with alpha particles generates much fewer $H\cdot$ and hydroxyl radicals than X- or

Pulse radiolysis

This technique makes it possible to characterize the chemical properties of free radicals derived either directly from the radiolysis of water or indirectly through reactions of these primary radicals with molecules present in the medium. Its principle consists in irradiating a solution for a very short time, from 10^{-9} to 10^{-6} seconds, using a pulsed particle accelerator, usually with electrons. These electrons, which are emitted in pulses, raise the kinetic energy of the radicals to several megaelectronvolts (MeV). When the irradiation is over the formation and disap-

pearance of the radicals is monitored by measuring the variation of their concentration with time using an optical method. As most of the radicals absorb light in the visible or, more often, in the ultraviolet range (wavelengths between $2\cdot 10^{-7}$ and $7.5\cdot 10^{-7}$ m) each radical can be identified by its absorption spectrum. Free radicals, the lifetime of which is sometimes as short as 10^{-7} s, are studied in the pulse radiolysis apparatus installed at CEA/Saclay (photo below).



Emmanuel Joly/CEA

gamma rays, and the recombination of hydrogen and hydrogen peroxide is incomplete.

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(4) Generic name of cyclic compounds in which two atoms of hydrogen on the ring are replaced by two atoms of oxygens.