

The Radiation Chemistry of water

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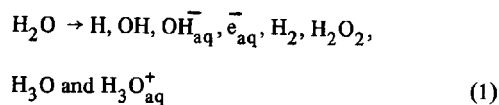
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Summary: The radiation chemistry of water is described. Primary processes in the radiolysis of liquid water, their time scale, yields of primary species at different pH values and their properties are given. Physical properties of hydrated electrons and rate constants for the reactions of primary species are also given.

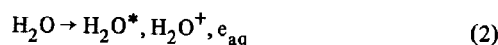
The unique importance of water has influenced its detailed investigations in the gaseous, liquid or solid state. The radiation studies of water¹⁻⁵ have contributed significantly towards an understanding of the reaction of water with matter. As a result of these studies in general, and of radiolysis of water in particular, the general mechanism of reaction resulting from the initial absorption of energy is easily understandable. The purpose of this article is to present an up-to-date version of the studies on radiolysis of water, from initial absorption of energy, to contribution of the radiolysis products of water, in radiation degradation of a model system, i.e., dilute aqueous solutions of carbohydrates.

Primary processes in radiolysis of water may be summarised as follows:



The course of events which accounts for the production of these species takes place when a fast moving particle passes through water. The consequential loss of energy gives rise to localised concentration of ions and radicals⁶⁻⁸. This was strongly supported by studies^{9,10} involving nanosecond pulse radiolysis technique which confirmed the localised concentration of the radicals produced. The conjuncture of ions and radicals which forms "spurs", "blobs" and "short tracks" depend on the energy of the fast moving particle. The theory of diffusion of these radicals from clusters has been discussed by Kuppermann⁶.

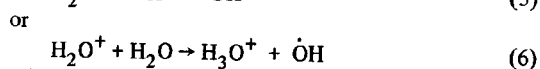
The ion pair, H_2O^+ and e_{aq} contributes significantly in the early stages of radiolysis of water:



The formation of excited water molecules takes place in the initial step. It is expected that they either ionize, or decompose into H atoms and OH radicals. They may also return to ground state by loss of energy:



The positive water ion fragments further into H^+ and OH. This takes place in 10^{-13} seconds:



The loss of energy by e^- takes place due to internal collision and when it reaches thermal energy level, it becomes what is known as hydrated electron, e_{aq} . This occurs in approximately 10^{-12} seconds.



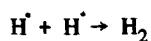
Table I gives approximate time scales for the radiolysis of liquid water¹:

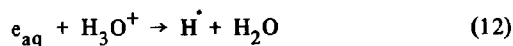
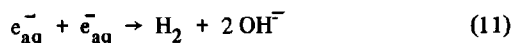
Since electrons, hydrogen atoms and hydroxyl radicals exist in close proximity to each other within the

Table 1. Approximate Time Scale for the Radiolysis of Liquid Water¹

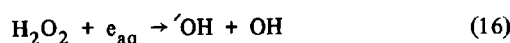
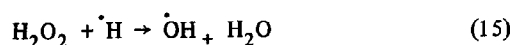
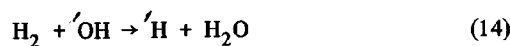
| Time (Secs.) | Event | Reaction |
|-------------------|---|--|
| 10 ⁻¹⁸ | Electron traverses approximately one molecular diameter. | $H_2O \rightarrow H_2O^+ + e^-$ |
| 10 ⁻¹⁵ | Time for vertical excitation to an electronic excited state. | $H_2O \rightarrow H_2O^*$ |
| 10 ⁻¹⁴ | Ion molecular reaction. Period for molecular vibration. | $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$ |
| 10 ⁻¹³ | Secondary electrons reduced to thermal energy by this time. | $H_3O^+ + e^- \rightarrow H + e^- \rightarrow H + H_2O$ |
| 10 ⁻¹² | Relaxation time for the dipole | |
| 10 ⁻¹¹ | Relaxation time for the dipole orientation of water. | $e^- \rightarrow \bar{e}_{aq}$ $e^- + H_2O \rightarrow H + OH_{aq}$ |
| 10 ⁻¹⁰ | Minimum time for diffusion controlled reaction in bulk liquid. | |
| 10 ⁻⁹ | Radiative life time of singlet excited states. | $H^{\cdot} + \dot{O}H \rightarrow H_2O$ $2^{\cdot}OH \rightarrow H_2O_2$ $2^{\cdot}H \rightarrow H_2$ $2e_{aq}^- \rightarrow H_2 + 2OH^-$ |
| 10 ⁻⁵ | Reaction time for radical with solute in molar concentration. | |
| 10 ⁻⁴ | Time required for a radical to diffuse interspur distance in track of 1 MeV energy state. | |
| 10 ⁻³ | Radiative lifetime of triplet excited state. | |
| 00 | Chemical reaction complete. | H_2, H_2O_2 and products of radical reactions with solute. |

blobs or spurs, they may recombine to produce H_2 , H_2O , H_2O_2 giving the molecular products, and OH^{\cdot} :





The presence of hydrogen in the system is responsible for the simultaneous destruction of these molecular products:



Yields of primary species:

Although there are as many as eight products (Eq. 1) which are produced by the radiolysis of water, the significant primary products are e_{aq}^- , H atoms and OH radicals^{5,11-18}. These three species are also identified in 184.9 nm photolysis of water¹⁹. The yields of formation of these species by radiolysis of water at different pH values are given in Table II:

Table 2. G value of primary species in radiolysis of water at low LET²⁰

| Species | pH values | | |
|-------------------------------|-----------|------|-------|
| | 0-2 | 4-11 | 13-14 |
| e_{aq}^- | — | 2.70 | 3.10 |
| H^\cdot | 3.65 | 0.55 | 0.54 |
| $\cdot\text{OH}$ | 2.95 | 2.80 | 2.90 |
| H_2 | 0.45 | 0.45 | 0.45 |
| H_2O_2 | 0.80 | 0.70 | 0.70 |
| H_3O^+ | — | 3.60 | — |
| OH^- | — | 1.00 | — |
| $-\text{H}_2\text{O}$ (Gross) | 5.00 | 5.00 | — |

Properties of primary species:

(i) *The hydrated electron, e_{aq}^- :*

The hydrated electron, e_{aq}^- , was first proposed by Frohlich and Platzman²¹. It is the major reducing species among the products of water radiolysis. It brings about a polarization in the surrounding water molecule dipole. Hence, a hydrated electron may be depicted as being located in the trap provided by the polarization.

The hydrated electrons can react with other hydrated electrons, water or cation:



Hence, hydrated electron is the conjugate base and is a very important species:



With molecular oxygen, hydrated electron produces $\cdot\text{O}_2^-$, which plays a significant role in radiolysis of aerated solutions:



Hydrated electrons react with N_2O and produce oxidizing radicals:



This reaction of N_2O is specific for electrons.

The reactions of hydrated electrons are therefore nucleophilic.

The important physical properties of hydrated electrons are given in Table III.

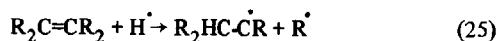
The hydrogen atom:

The hydrogen atom is not the major reducing species produced by the radiolysis of water. With organic compounds it is involved in hydrogen atom abstraction re-

Table III. Physical Properties of hydrated electron, e^{-2}_{aq}

| | |
|-------------------------------------|------------------------------------|
| λ max | 720.0 nm (1.72 eV) |
| ϵ 720 nm | 15,800 $M^{-1}cm^{-1}$ |
| pK | 9.7 |
| Charge | -1.0 |
| Diffusion constant | $4.5 \times 10^{-5} cm^2 sec^{-1}$ |
| f = Oscillator strength | 0.80 |
| G(e^{-2}_{aq}) in neutral water | 2.60 |
| Half-life in water | 800 μ secs. |
| Mean radius of charge distribution | 2.5 - 3.0 Å |

actions and double bond or ring addition²³:



With aromatic compounds like aniline, nitrobenzene and

the benzoate ion it acts as an electrophilic reagent. In pH 0-7, the hydrogen atoms are formed by reactions of hydrated electrons with protons, (Eqn. 18). With molecular oxygen, hydrogen atom gives hydroperoxyl radicals:



The hydroxyl radical, $\dot{O}H$:

Hydroxyl radical is the major oxidising species produced by radiolysis of water. Since its optical absorption is very weak ($\lambda_{760 nm} = 370 M^{-1} cm^{-1}$), many of its reaction rate constants have been determined by competition methods. Indirect evidence of the existence of hydroxyl radicals has been provided by hydroxylation of aqueous acrylonitrile, following gamma irradiation²⁴.

The main reactions of hydroxyl radicals are atom abstraction, radical addition, and electron transfer.

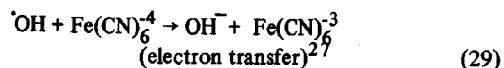
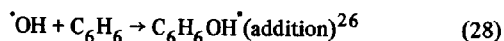
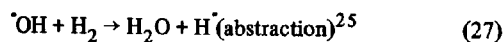
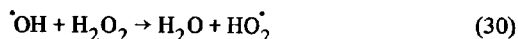


Table IV. Rate constants in pulse radiolysed water²⁹

| Reaction | Rate constant ($M^{-1}sec^{-1}$) | pH | | |
|---------------------------|------------------------------------|---------------------------|-------------------------------|---------|
| $e^{-} + H_2O$ | --- | $H^{\bullet} + OH_{aq}$ | 16 ± 1 | 8.4 |
| $e^{-}_{aq} + e^{-}_{aq}$ | --- | $H_2 + 2OH^{\bullet}$ | $0.9 \pm 0.15 \times 10^{10}$ | 10.9 |
| $e^{-} + H_3O^{+}$ | --- | $H^{\bullet} + H_2O$ | 1.1 ± 0.15 | 13.3 |
| | | | 2.07 ± 10^{10} | 2.1-4.3 |
| $e^{-} + H_2O_2$ | --- | $\dot{O}H + OH^{\bullet}$ | 1.23×10^{10} | 7.0 |
| $H + H$ | --- | H_2 | 2.0×10^{10} | 2.1 |
| $H^{\bullet} + \dot{O}H$ | --- | H_2O | $0.7-3.2 \times 10^{10}$ | 3.0 |
| $H^{\bullet} + H_2O_2$ | --- | $\dot{O}H + H_2O$ | 9.0×10^7 | 2.1 |
| $\dot{O}H + \dot{O}H$ | --- | H_2O_2 | 1.26×10^{10} | 7.0 |
| $\dot{O}H + H_2O_2$ | --- | $H_2O + H_2O$ | 4.5×10^{10} | 7.0 |
| $OH^{\bullet} + H_3O^{+}$ | --- | $2 H_2O$ | 1.43×10^{11} | 7.0 |

The hydroperoxyl radical, HO₂[•]:

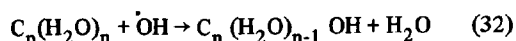
Another of the significant species produced by the radiolysis of water is hydroperoxyl radical, HO₂[•], which, is most likely produced by the reaction²⁸:



HO₂[•] is as strong as organic acids and has a pK of 4.4. In neutral solutions it is present as O₂⁻:

*Radiolysis of carbohydrates:*

Recent studies on γ -radiolysis of dilute aqueous solutions of carbohydrates indicate the formation of radiolysis products of solvent water, and their participation in the degradation of carbohydrates, via carbohydrate free radicals. These free radicals are produced by simultaneous radiolysis of carbohydrate molecules³⁰⁻³³:

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