RADIATION CHEMISTRY OF LIQUID SYSTEMS

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1. INTRODUCTION

The radiation chemistry of liquid systems illustrates a versatile use of high energy ionizing radiation [1-4]. Radiolysis, the initiation of reactions by high energy radiation, is a very valuable and powerful chemical tool for inducing and studying radical reactions in liquids. In many cases radiolysis offers a convenient and relatively easy way of initiating radical reactions in all phases (including liquid phase) that cannot be or can be performed with some limitations by chemical, electrochemical and photolytic methods. Radiolysis of most liquids produces solvated electrons and relatively simple free radicals, some of which can oxidize and/or reduce materials [5]. This chapter is divided into four main sections: "Introduction", "Radiolysis of water", "Radiolysis of organic solvents", and "Radiolysis of ionic liquids". The first section summarizes the mechanisms and features of radiation energy deposition along with a quantification of chemical effects induced by radiation, and techniques used in radiation chemical studies. The second section focuses on radiation-induced radical reactions in water and aqueous solutions using low and high linear energy transfer (LET) irradiation at ambient and high temperatures, and high pressures. Relevant examples include radical reactions initiated by primary and secondary radicals from water radiolysis with a variety of compounds. The third section describes the most important features of radiolysis in organic liquids using common solvents for inducing and studying radical reactions. Relevant examples include radical reactions connected with the selective formation of radical cations, radical anions and excited states. The last section briefly summarizes the most commonly use ionic liquid (IL) systems and highlights radiation-induced radical reactions in IL, a new matrix used for the radiation generation of radicals and radical ions in the liquid phase [6].

The chemical changes that commonly involve radiation-induced radical reactions are the consequences of the absorption of energy of high energy radiation by matter [7-13].

1.1. MECHANISMS OF RADIATION ENERGY DEPOSITION

The mechanisms by which radiation energy is deposited in matter depend upon the type of radiation. There are three types of ionizing radiation: (i) electromagnetic radiation (X- and γ-rays), (ii) charged particles (electrons and heavy positive ions), and (iii) neutral particles (neutrons). There are three important processes by which electromagnetic radiation interacts with matter. These processes are the photoelectric effect, the Compton effect, and pair production, probabilities of which vary with the energy of radiation and the atomic number, Z, of the material involved [7-13]. Charged particles interact with matter *via* three main processes, *i.e.* emission of "bremsstrahlung" or braking radiation, inelastic and elastic collisions. Their relative importance depends upon the energy of the particles and also on the nature of the material which they pass through (see Chapter 2). In the case of neutrons there are four main processes by which they interact in collisions with atomic nuclei: elastic and inelastic scatterings, nuclear reactions, and neutron capture.

The absorption of the energy in a medium, M, causes ionization of molecules and/or formation of excited and super-excited states represented by Eqs. (1) and (2), respectively:

$$M \xrightarrow{\;\wedge\wedge\wedge\wedge\;} M^{\bullet+} + e^- \tag{1}$$
$$M \xrightarrow{\;\wedge\wedge\wedge\wedge\;} M^*/M^{**} \tag{2}$$

The electrons produced in ionization (Eq. (1)) can cause further ionization and excitation. Thus, the primary effect of any type of ionizing radiation on matter is the production of radical ions, ions, excited states and electrons [14].

1.2. FEATURES OF RADIATION ENERGY DEPOSITION

Radiation energy deposition is spatially inhomogeneous and creates sites of dense ionization, called spurs. The mean rate of energy loss by a particle per unit path length, called linear energy transfer (LET), increases in the sequence of electron, proton and α-particle, for the same particle energy, E. This is, according to the Bethe equations, because the value of LET increases with decreasing particle velocity, v, which decreases with increasing particle mass, M, for the same E since LET increases as the square of the particle charge, Z [11, 15-17]. At sub-picoseconds time scales, local inhomogeneous distribution of ions and radical ions, excited states and electrons in small and widely separated volumes called spurs are produced by high energy electromagnetic ra-

diation or by the charged particles (including electrons) resulting in a high local concentration of reactive species (ion pairs) and promoting their recombination. In liquids, the fate of ion pairs is strongly dependent on the properties of the liquid. In non-polar liquids (*e.g.* hydrocarbons), characterized by low permittivity, most of the ejected electrons return to the initiating radical cation. On the other hand, in polar liquids (water, alcohols) most of the ejected electrons have sufficient energy to escape from the positive radical ions and, after thermalization (loss of their excess energy), are trapped by surrounding molecules forming solvated electrons (e^-_{solv}) [5].

An important feature of high energy radiation is also its non-selective absorption in matter. This means that molecules are ionized according to their relative abundance in the irradiated medium, *i.e.* partition of energy among the components of a sample is controlled by the contribution of each component and to the density of electrons. The concept of a direct effect of the radiation on the solute and an indirect effect, in which excited states and ions derived from the solvent subsequently react with the solute refers to this phenomenon. In studies of dilute solutions, any direct effect on the solute molecules will be negligible in comparison with the indirect effect. The radiolysis mechanisms of the solvent are of paramount importance for radical reactions initiated by high energy radiation. The radical reactions observed are essentially those resulting from the interactions of excited states and/or ions from the solvent with themselves, or with any solute present. One potential disadvantage of the latter situation is that the limiting rate of intermediate formation derived from the solute is usually controlled by its concentration.

1.3. QUANTIFICATION OF RADIATION CHEMICAL EFFECTS

Radiation chemical effects are quantified by the radiation chemical yield, G(X) [18], defined as the quotient of the amount n(X) of a substance X, either produced or destroyed and the energy, E, absorbed in the medium (Eq. (3)):

$$G(X) = n(X)/E \qquad (3)$$

The SI unit of the G-value is $mol \cdot J^{-1}$. For practical purposes $\mu mol \cdot J^{-1}$ unit is used. In the earlier literature, the G-values were expressed as the number of molecules produced or destroyed per 100 eV of energy absorbed. The mutual conversions of these units are as follows:

$$1 \ \mu mol \cdot J^{-1} = 9.65 \ \text{molecules} \ (100 \ eV)^{-1}$$
$$1 \ \text{molecule} \ (100 \ eV)^{-1} = 0.1036 \ \mu mol \cdot J^{-1}$$

Since the absorbed fraction of the radiation energy can only induce physical and chemical changes, the absorbed energy (the absorbed dose) is an important parameter. The absorbed dose (dose), D, is defined as the mean energy, dE, deposited in an incremental quantity of matter, divided by the mass of that matter (Eq. (4)):

$$D = dE/dm \qquad (4)$$

The preferred SI unit of the absorbed dose is the gray (Gy) which expresses the energy in joules (J) absorbed in the unit mass – kg: 1 Gy = 1 J·kg^{-1}. The former unit of the absorbed unit, rad, was defined as 100 erg·g^{-1}. Hence, 1 Gy = 100 rad.

1.4. TECHNIQUES OF RADIATION CHEMISTRY

Two main types of approaches are commonly used in applying radiation chemistry to investigate radical reactions in liquids. First, radiolysis can involve exposure to a steady radiation source, usually a ^{60}Co source for a desired amount of time and the stable products are analyzed after the end of the radiolysis period. Modern analytical techniques (including high performance liquid chromatography for separation of products, with spectrophotometric, fluorescence, electrochemical, mass spectrometric or nuclear magnetic resonance detections) are used for qualitative and quantitative determination of the final products [5, 19].

The second approach involves exposure of a selected chemical system to pulsed sources, usually electron accelerators, where sufficiently high concentration of radicals is desired in a short time in order to follow their reactions directly [5, 19]. This technique, pulse radiolysis, has been the main source of a quantitative information concerning reaction kinetics of free radicals in solutions [20-24]. For radicals in solutions the most common used technique is time-resolved UV-Vis spectroscopy [22, 23, 25], but time-resolved conductivity [23, 26], electron paramagnetic resonance [27], vibrational resonance Raman spectroscopy [28], microwave absorption spectroscopy [29], polarography [30], circular dichroism [31], and recently infrared spectroscopy [32], although less widely employed, can also provide kinetic, spectral, and mechanistic details that are not accessible *via* optical measurements.

Due to space limitations, a comprehensive overview of basics of radiation--induced phenomena in liquids cannot be given here. There are many excellent and comprehensive discussions of this [7, 10, 12, 33-35], and books which address the topics mentioned above in a more detailed manner [11, 13, 15, 36-40].

2. RADIOLYSIS OF WATER

The radiolysis of water has been studied extensively since the beginning of radiation chemistry. Excellent critical reviews of the spectral and kinetic properties, methods of production, and compilations of reaction rate constants of

the primary water radiolysis transients with inorganic and organic substrates have been written over the years [2, 11, 18, 41-49]. Most of radiation-induced radical reactions have been studied in aqueous solutions because they are readily available and not difficult to work with. Moreover, the radiolysis of water is a relatively easy and convenient way to produce an enormous variety of highly reactive radical species which otherwise cannot readily be generated by thermal or photochemical methods. There were several motivations for undertaking and pursuing these studies: (i) to gain a knowledge about chemical processes in general (*e.g.* redox and polymerization processes); (ii) to understand effect of high energy radiation on biologically relevant molecules (water is a main constituent in living organisms and plays a key role in biological systems); (iii) to produce and study the reactions of reactive short-lived species that are also produced in living organisms, *e.g.* hydroxyl radicals ($^{\bullet}$OH), peroxyl radicals (ROO$^{\bullet}$), and superoxide radical anions ($O_2^{\bullet-}$); and (iv) to control and predict precisely effects of water radiolysis in water cooled nuclear reactors in order to avoid unwanted effects such as radiation-induced stress corrosion cracking.

2.1. RADIOLYSIS OF WATER AT AMBIENT TEMPERATURES WITH LOW LET IRRADIATION

2.1.1. Primary transients: formation, spur reactions, radiation chemical yields, acid-base equilibria, spectral and redox properties

Formation of the radical cation ($H_2O^{\bullet+}$) and pre-hydrated electrons (e^-_{prehyd}) is a consequence of the ionization of water molecules and represents the primary process in the radiolysis of water (Eq. (5)). There is no unequivocal evidence that electronic excitation of water molecules (Eq. (6)) plays any significant role in radiolysis.

$$H_2O \xrightarrow{\wedge\wedge\wedge\wedge\wedge} H_2O^{\bullet+} + e^-_{prehyd} \tag{5}$$

$$H_2O \xrightarrow{\wedge\wedge\wedge\wedge\wedge} H_2O^* \tag{6}$$
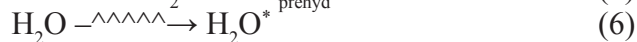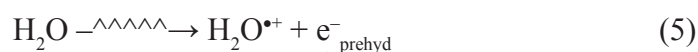
Both reactions occur on the time scale of electronic transition, *i.e.* ~10^{-16} s. The water radical cation ($H_2O^{\bullet+}$) is a very strong acid and immediately loses a proton (in ~10^{-14} s) to neighboring water molecules forming hydroxyl radical (Eq. (7)):

$$H_2O^{\bullet+} + H_2O \rightarrow {}^{\bullet}OH + H_3O^+ \tag{7}$$

The lifetime of $H_2O^{\bullet+}$ was recently measured to be around 200 fs using polarization anisotropy technique [50]. The yield of $H_2O^{\bullet+}$ at few tens of fs was estimated to be around 0.53 μmol·J^{-1} [51]. The electronically excited water molecules (H_2O^*) may undergo homolytic dissociation (Eq. (8)) in ~10^{-13} s and the electrons ejected in an ionization process (Eq. (5)) undergo hydration by ~10^{-12} s, after thermalization (Eq. (9)):

$$H_2O^* \rightarrow {}^{\bullet}H + {}^{\bullet}OH \tag{8}$$

$$e^-_{prehyd} + nH_2O \rightarrow e^-_{aq} \tag{9}$$

At this time, the products of reactions depicted in Eqs. (7)-(9) are distributed inhomogeneously and located together in spurs. Subsequently, these products start to diffuse randomly. Some of them interact with one another within spurs, before diffusing apart into the bulk water, forming molecular and secondary radical products. These spur reactions (Eqs. (10)-(17)) together with their respective rate constants are listed in Table 1.
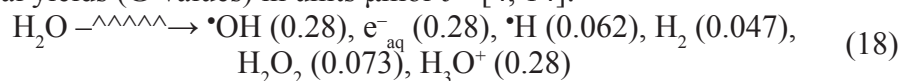
Table 1. Spur reactions in water and their rate constants [46].

Spur reaction (number)	$k \ [dm^3 \cdot mol^{-1} \cdot s^{-1}]$
$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2^-OH \ (10)^a$	5.4×10^9
$e^-_{aq} + {}^\bullet OH \rightarrow {}^-OH \ (11)$	3.0×10^{10}
$e^-_{aq} + H_3O^+ \leftrightarrows {}^\bullet H + H_2O \ (12)$	2.3×10^{10}
$e^-_{aq} + {}^\bullet H \rightarrow H_2 + {}^-OH \ (13)^a$	2.5×10^{10}
${}^\bullet H + {}^\bullet H \rightarrow H_2 \ (14)$	1.3×10^{10}
${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \ (15)$	5.3×10^9
${}^\bullet OH + {}^\bullet H \rightarrow H_2O \ (16)$	3.2×10^{10}
$H_3O^+ + {}^-OH \rightarrow 2H_2O \ (17)$	1.4×10^{11}

[a] The mass balance is ensured by hydration water.

Those products, which diffuse outside the spurs, become homogeneously distributed and may react with added solutes (acting as scavengers). All spur reactions and diffusion of reactants leading to their homogeneity are completed within 10^{-7} s.

The radiolysis of water (for low LET irradiation ~0.23 eV·nm^{-1}) is summarized by Eq. (18), where the numbers in parentheses represent radiation chemical yields (G-values) in units μmol·J^{-1} [4, 14]:

$$H_2O \xrightarrow{\wedge\wedge\wedge\wedge\wedge} {}^\bullet OH \ (0.28), \ e^-_{aq} \ (0.28), \ {}^\bullet H \ (0.062), \ H_2 \ (0.047), \tag{18}$$
$$H_2O_2 \ (0.073), \ H_3O^+ \ (0.28)$$

The primary transients from water radiolysis (Eq. (18)) are involved in the following acid-base equilibria represented by Eqs. (19) and (20):

$$^\bullet H + HO^- \leftrightarrows e^-_{aq} + H_2O \tag{19}$$
$$^\bullet OH + HO^- \leftrightarrows O^{\bullet-} + H_2O \tag{20}$$

Hydrogen atoms (${}^\bullet H$) and hydrated electrons (e^-_{aq}) exist in the acid-base equilibrium (Eq. (19)) with $pK_a = 9.1$ (${}^\bullet H$ atom is a conjugate acid of e^-_{aq}). The lifetime of e^-_{aq} in pure water is quite long since its protonation by water is slow. However, at pH < 4, the diffusion-controlled reaction of e^-_{aq} with bulk protons (Eq. (12), Table 1) is important in causing an increase of the yield of ${}^\bullet H$ atoms

with decreasing pH and thus their radiation chemical yield in acidic solutions can be as high as 0.34 µmol·J^{-1}. On the other hand, in very basic solutions $^\bullet$H atoms are converted into e^-_{aq} with $k_{forward}$ (in equilibrium represented by Eq. (19)) = 2.2×10^7 dm^3·mol^{-1}·s^{-1} [46].

Hydroxyl radicals ($^\bullet$OH) exist in the acid-base equilibrium (Eq. (20)) with pK$_a$ = 11.8 ($^\bullet$OH is a conjugate acid of the oxide radical ion (O$^{\bullet-}$)), with $k_{forward}$ (in equilibrium represented by Eq. (20)) = 1.3×10^{10} dm^3·mol^{-1}·s^{-1} and $k_{reverse}$ (in equilibrium represented by Eq. (20)) = 7.9×10^7 s^{-1} [52]. Since O$^{\bullet-}$ radical anion is very rapidly protonated by water, its radical reactions occur in a significant extent only at a pH > 12.

Spectral properties of the primary transients from water radiolysis are summarized in Table 2.

Table 2. Spectral parameters and reduction potentials of primary transients in water radiolysis [49, 53].

Transient	λ_{max} [nm]	ε_{max} [dm^3·mol^{-1}·cm^{-1}] [49]	E^0 *vs.* NHE [V] [53]
$^\bullet$OH	230	530	+2.72 (for the redox couple: $^\bullet$OH, H$^+$/H$_2$O) +1.90 (for the redox couple: $^\bullet$OH/$^-$OH)
O$^{\bullet-}$	240	240 (for pH 13)	+1.78 (for the redox couple: O$^{\bullet-}$, H$_2$O/2$^-$HO)
e^-_{aq}	720	19 000	−2.87
$^\bullet$H	< 200	1 620 (for λ_{max} = 188 nm)	−2.31

The hydrated electron is characterized by its strong absorption at 720 nm and the majority of oscillating strength is derived from optical transitions from the equilibrated *s* state to the *p*-like excited state. The 720-nm absorption is used for the determination of reaction rate constants with the vast variety of compounds. On the other hand, both the $^\bullet$H atoms and $^\bullet$OH(O$^{\bullet-}$) radicals absorb in the far UV region, which has made their distinction and observation very difficult, if not impossible. Therefore, their reaction rate constants with the variety of compounds have been determined either by observation of the respective products or competition techniques [46].

Redox properties of the primary transients from water radiolysis can be summarized as follows: (i) the $^\bullet$OH radical is a powerful one-electron oxidant with a reduction potential varying with the pH, (ii) the hydrated electron is a

powerful reductant in neutral and alkaline solutions while the $^\bullet$H atom becomes the major reductant in acidic solutions [46, 53].

The radical cation $H_2O^{\bullet+}$ absorbs light in the visible spectral domain [54], and its reduction potential has been estimated as $\sim +4.0$ V *vs.* NHE [51].

### 2.1.2. Selective generation of primary transients

Since the primary transients formed in the radiolysis of aqueous solutions are characterized either by oxidizing ($^\bullet$OH) or reducing (e^-_{aq}, $^\bullet$H) properties, it is desirable to study their reactions in conditions when only one type of radical is present. These conditions can be achieved *via* an appropriate design of the reaction system which subsequently will be exposed to high energy irradiation [18].

To eliminate the contribution of e^-_{aq} in the reaction system, the solution is saturated with nitrous oxide (N_2O). Hydrated electrons are rapidly scavenged by N_2O generating additional amount of $^\bullet$OH radicals (Eq. (21)) with $k_{21} = 9.1 \times 10^9$ dm$^3\cdot$mol$^{-1}\cdot$s^{-1} [55], and thus yield amounts to 0.56 µmol$\cdot$J^{-1}.

$$e^-_{aq} + N_2O \rightarrow N_2 + O^{\bullet-} (+ H_2O) \rightarrow N_2 + {}^\bullet OH + {}^-OH \qquad (21)$$
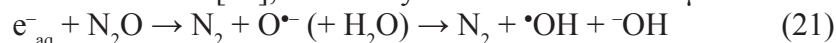
The $^\bullet$H atoms react slowly with N_2O ($k = 2.1 \times 10^6$ dm$^3\cdot$mol$^{-1}\cdot$s^{-1}) [4], and therefore in these solutions their reactions are not eliminated. However, the yield of $^\bullet$H atoms represents $\cong 10\%$ of the total yield of radicals at neutral solutions.

A convenient way to study reactions of e^-_{aq} (without a contribution of $^\bullet$OH radicals) is irradiation of deaerated neutral aqueous solutions (with Ar/N_2) containing high concentration (> 0.1 M) of 2-methyl-2-propanol (*tert*-butanol). The $^\bullet$OH radicals are selectively scavenged by *tert*-butanol forming 2-hydroxy-2,2-dimethyl radical with $k = 6.0 \times 10^8$ dm$^3\cdot$mol$^{-1}\cdot$s^{-1} (Eq. (22)) [46]:

$$^\bullet OH + (CH_3)_3C–OH \rightarrow H_2O + {}^\bullet CH_2(CH_3)_2C–OH \qquad (22)$$
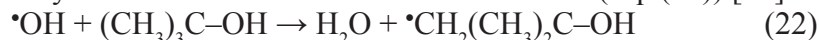
The yield of $^\bullet$H atoms is almost not affected since their rate constant with *tert*-butanol is low ($k = 1.7 \times 10^5$ dm$^3\cdot$mol$^{-1}\cdot$s^{-1}) [46], and recently noted at 1.15×10^6 dm$^3\cdot$mol$^{-1}\cdot$s^{-1} [56]. The $^\bullet CH_2(CH_3)_2C–OH$ formed is nearly unreactive due to steric hindrance, its optical absorption band is located < 270 nm and, in principle, does not interfere with other radicals. The irradiated system contains only e^-_{aq} and $^\bullet$H atoms with the respective radiation chemical yields 0.28 and 0.062 µmol$\cdot$J^{-1}.

The "cleanest" way to study $^\bullet$H-atoms reactions (without a contribution of $^\bullet$OH radicals and e^-_{aq}) is irradiation of highly acidic aqueous solutions saturated with H_2. The $^\bullet$OH radicals react with H_2 generating additional amount of $^\bullet$H atoms (Eq. (23)) with $k_{23} = 4.2 \times 10^7$ dm$^3\cdot$mol$^{-1}\cdot$s^{-1} [46]:

$$^\bullet OH + H_2 \rightarrow H_2O + {}^\bullet H \qquad (23)$$

This approach, due to the low solubility of H_2 under normal pressure conditions, has not found a practical use (a special pressure cell is needed). Therefore, $^\bullet$H-atoms reactions can be routinely studied by irradiations of highly acidic Ar/N_2-saturated aqueous solutions containing high concentration (> 0.1 M) of *tert*-butanol. The $^\bullet$OH radicals are removed in reaction (Eq. (22)) and e^-_{aq} are

converted to $^\bullet$H atoms *via* reaction with H_3O^+ (Eq. (12), Table 1), and thus their radiation chemical yield amounts to 0.34 μmol·J^{-1}.

2.1.3. Generation of transients in aerated and O_2-saturated aqueous solutions: formation, acid-base equilibria, spectral, kinetic, and redox properties
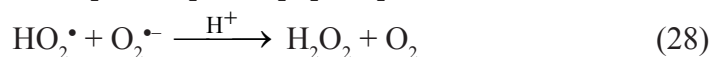
In aerated and O_2-saturated aqueous solutions both $^\bullet$H atoms and e^-_{aq} react with molecular oxygen (O_2) according to reactions (Eqs. (24) and (25)) with $k_{24} = 2.1 \times 10^{10}$ dm^3·mol^{-1}·s^{-1} and $k_{25} = 1.9 \times 10^{10}$ dm^3·mol^{-1}·s^{-1} [46]:

$$^\bullet H + O_2 \rightarrow HO_2^\bullet \tag{24}$$
$$e^-_{aq} + O_2 \rightarrow O_2^{\bullet-} \tag{25}$$

Perhydroxyl radicals ($HO_2^\bullet$) and superoxide radical anions ($O_2^{\bullet-}$) exist in the acid-base equilibrium (Eq. (26)) with pK_a = 4.88 ($HO_2^\bullet$ radical is a conjugate acid of $O_2^{\bullet-}$ radical anion) [57].

$$HO_2^\bullet \leftrightarrows H^+ + O_2^{\bullet-} \tag{26}$$

$HO_2^\bullet$ and $O_2^{\bullet-}$ radicals undergo disproportionation reaction *via* a pH-dependent mechanism that involves equilibrium (Eq. (26)) and reactions (Eqs. (27) and (28)):

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \tag{27}$$

$$HO_2^\bullet + O_2^{\bullet-} \xrightarrow{H^+} H_2O_2 + O_2 \tag{28}$$

$$O_2^{\bullet-} + O_2^{\bullet-} \rightarrow \text{no reaction} \tag{29}$$

The values of k_{27} and k_{28} of 8.3×10^5 dm^3·mol^{-1}·s^{-1} and 9.7×10^7 dm^3·mol^{-1}·s^{-1} were calculated by fitting the experimental data of the observed rates of disproportionation at varying pH taking into account Eqs. (27)-(29) [57].

Radiolysis of water at pH > 6 in the presence of O_2 and formate ions (HCO_2^-) leads to the exclusive formation of $O_2^{\bullet-}$ *via* reactions depicted in Eqs. (24)-(26), (30) and (31):

$$^\bullet OH + HCO_2^- \rightarrow CO_2^{\bullet-} + H_2O \tag{30}$$
$$CO_2^{\bullet-} + O_2 \rightarrow O_2^{\bullet-} + CO_2 \tag{31}$$
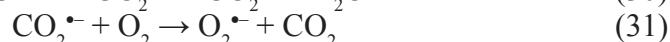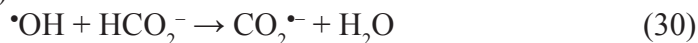
Interestingly, $^\bullet$OH radical is unreactive towards O_2, however, its conjugate base, the oxide radical anion ($O^{\bullet-}$) react with O_2 (Eq. (32)) forming ozonide radical anion ($O_3^{\bullet-}$):

$$O^{\bullet-} + O_2 \leftrightarrows O_3^{\bullet-} \tag{32}$$

These two radicals exist in an equilibrium with $k_{32} = 3.0 \times 10^9$ dm^3·mol^{-1}·s^{-1} [46], and $k_{-32} = 3.3 \times 10^3$ s^{-1} [58].

The ozonide radical anion is characterized by its absorption at 430 nm which has been used for determination of its reaction rate constants with radicals [59, 60]. Both the $HO_2^\bullet$ and $O_2^{\bullet-}$ radicals absorb in the far UV region, which made their distinction and observation very difficult, if not impossible (Table 3). Their reaction rate constants with the variety of compounds were determined either by observation of the respective products or competition techniques.

Table 3. Spectral parameters and reduction potentials of transients formed during radiolysis of aerated and oxygenated water [49, 53].
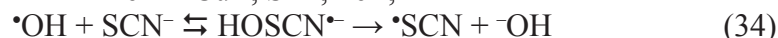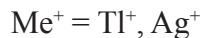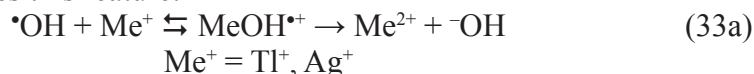
Transient	λ_{max} [nm]	ε_{max} [dm^3·mol^{-1}·cm^{-1}] [49]	E^0 *vs.* NHE [V] [53]
HO$_2^\bullet$	225 (for pH 1.5)	1400 (for pH 1.5)	+1.48 (for the redox couple: HO$_2^\bullet$, H$^+$/H$_2$O$_2$) +0.79 (for the redox couple: HO$_2^\bullet$/HO$_2^-$)
O$_2^{\bullet-}$	245 (for pH 10.5)	2350 (for pH 10.5)	−0.33 (for the redox couple: O$_2$/O$_2^{\bullet-}$) +1.03 (for the redox couple O$_2^{\bullet-}$, H$^+$/HO$_2^-$)
O$_3^{\bullet-}$	430 (for pH 13.1)	1900 (for pH 13.1)	+1.01 (for pH 11-12; for the redox couple: O$_3$/O$_3^{\bullet-}$)

Redox properties of these transients can be summarized as follows: the HO$_2^\bullet$ and O$_2^{\bullet-}$ radicals are mild one-electron oxidants with a reduction potential varied with the pH (Table 3).

2.1.4. Radical reactions involving primary transients

$^\bullet$*OH radicals.* The $^\bullet$OH radical undergoes the following types of reactions: (i) electron transfer (ET); (ii) hydrogen atom abstraction; (iii) addition to C=C, C=N and C=S bonds; (iv) addition to aromatic rings; and (v) addition to electron-rich functional groups [45]. These reactions reflect *inter alia* its electrophilic character [61], and strong oxidizing properties. Rate constants for thousands of reactions of $^\bullet$OH radicals have been compiled, including reactions with molecules, ions, and radicals derived from inorganic and organic solutes [46].

In most ET reactions, formation of an $^\bullet$OH adduct precedes the actual ET reaction. Oxidation of metal ions (Eqs. (33a) and (33b)) and inorganic anions (Eq. (34)) illustrates this feature:

$$^\bullet\text{OH} + \text{Me}^+ \leftrightharpoons \text{MeOH}^{\bullet+} \rightarrow \text{Me}^{2+} + {}^-\text{OH} \qquad (33a)$$
$$\text{Me}^+ = \text{Tl}^+, \text{Ag}^+$$
$$^\bullet\text{OH} + \text{Me}^{2+} \leftrightharpoons \text{MeOH}^{\bullet 2+} \rightarrow \text{Me}^{2+} + {}^-\text{OH} \qquad (33b)$$
$$\text{Me}^{2+} = \text{Cu}^{2+}, \text{Sn}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}$$
$$^\bullet\text{OH} + \text{SCN}^- \leftrightharpoons \text{HOSCN}^{\bullet-} \rightarrow {}^\bullet\text{SCN} + {}^-\text{OH} \qquad (34)$$
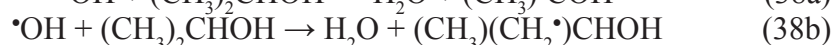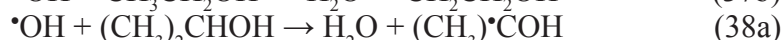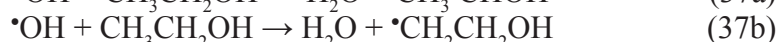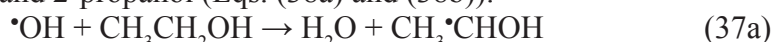
A driving force for H-abstraction reactions by $^\bullet$OH radicals is that the H–OH bond dissociation energy (BDE) is very high (111 kcal·mol^{-1}), while the BDEs

of the C–H and S–H bonds are usually much weaker. Reactions of $^\bullet$OH radicals with methanol (BDE H–CH$_2$ = 103 kcal·mol^{-1}) (Eq. (35)) and methanethiol (BDE S–H = 85 kcal·mol^{-1}) (Eq. (36)) confirm this:

$$^\bullet OH + CH_3OH \rightarrow H_2O + {}^\bullet CH_2OH \qquad (35)$$
$$^\bullet OH + CH_3SH \rightarrow H_2O + CH_3S^\bullet \qquad (36)$$

Since the BDE for primary hydrogens (H–CH$_2$) is higher than for the secondary (>CH–H) (98 kcal·mol^{-1}) and tertiary (>C–H) (95 kcal·mol^{-1}), a remarkable selectivity is observed for the H-abstraction reactions in ethanol (Eqs. (37a) and (37b)) and 2-propanol (Eqs. (38a) and (38b)):

$$^\bullet OH + CH_3CH_2OH \rightarrow H_2O + CH_3{}^\bullet CHOH \qquad (37a)$$
$$^\bullet OH + CH_3CH_2OH \rightarrow H_2O + {}^\bullet CH_2CH_2OH \qquad (37b)$$
$$^\bullet OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2{}^\bullet COH \qquad (38a)$$
$$^\bullet OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)(CH_2{}^\bullet)CHOH \qquad (38b)$$

The yields (in %) of H-abstraction reactions (Eqs. (37a) and (38a)) are equal to 84.3 and 85.5%, respectively. The yields of H-abstraction reactions (Eqs. (37b) and (38b)) amounts only to 13.3% [62].

Addition of $^\bullet$OH radicals to C=C double bonds (Eq. (39)) is very fast and occurs close to diffusion-controlled rates (*e.g.* in ethylene k$_{39}$ = 4.4 × 10^9 dm^3·mol^{-1}·s^{-1}):

$$^\bullet OH + H_2C{=}CH_2 \rightarrow {}^\bullet CH_2{-}CH_2{-}OH \qquad (39)$$

Addition will be the preferential way over H-abstraction, even in the molecules having weakly bound hydrogen atoms, such as pentadienylic in 1,3- and 1,4-cyclohexadienes and allylic ones in thymine.

Addition of $^\bullet$OH radicals to C=N double bonds was observed in purines (guanine and adenine, two of the bases in deoxyribonucleic acid, DNA). The C(8)–OH adducts are formed with the yield of 17 and 37%, respectively, and both radicals possess reducing properties [45].

Addition of $^\bullet$OH radicals to S=O double bonds occurs in sulfoxides and the resulting radical undergoes a very rapid β-fragmentation leading, in the case of dimethyl sulfoxide, to the methide radical (Eq. (40)) [63]:

$$^\bullet OH + (CH_3)_2S{=}O \rightarrow (CH_3)_2S(OH){-}O^\bullet \rightarrow {}^\bullet CH_3 + CH_3S({=}O){-}OH \quad (40)$$
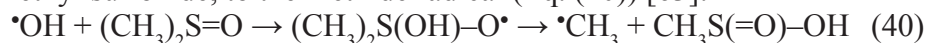
Addition of $^\bullet$OH radicals to aromatic rings leads to a short-lived π-complex (being in an equilibrium with substrates) prior to transformation into σ-complex, where the OH substituent bounds tightly to the carbon atoms (Eq. (41)):

$$(41)$$
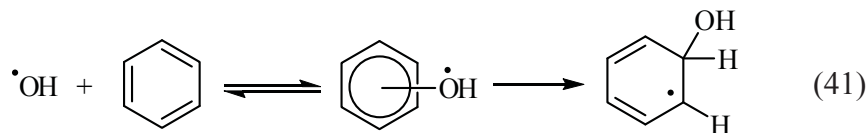
Electron-donating substituents (*e.g.* –OCH$_3$, –OH) in the aromatic ring direct $^\bullet$OH radicals into the *ortho*- and *para*-positions, while electron-withdrawing substituents (–NO$_2$) mostly into the *meta*-position. In the case of neutral substituents (–COOH), there is no preference for the site of addition, and an even distribution of isomers is observed [64].

Addition of $^\bullet$OH radicals to electron-rich functional groups was observed in sulfides and disulfides [65]. In the case of sulfides, the OH-adduct undergoes, depending on the pH, either proton-catalyzed hydroxide ion ($^-$OH) elimination (Eq. (42a)) or spontaneous dissociation (Eq. (42b)), both processes lead to formation of the monomeric sulfur radical cation:
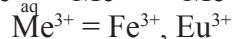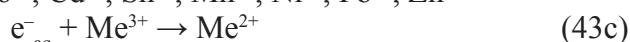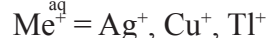
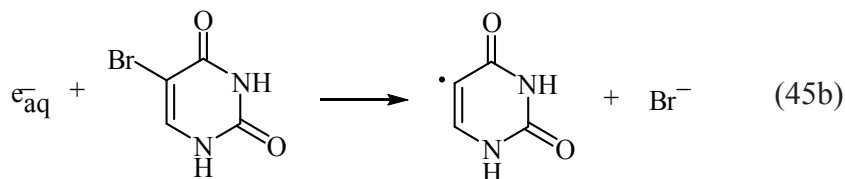$$^\bullet OH + R-S-R \rightarrow R-S^\bullet(-OH)-R \xrightarrow{\;H^+\;} R-S^{\bullet+}-R + H_2O \qquad (42a)$$

$$^\bullet OH + R-S-R \rightarrow R-S^\bullet(-OH)-R \rightarrow R-S^{\bullet+}-R + {}^-OH \qquad (42b)$$
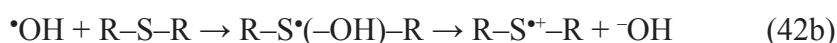
These radical cations undergo either deprotonation at neighboring carbon atoms forming α-(alkylthio)alkyl radicals or can be stabilized by 2c-3e bonding with other heteroatoms (*e.g.* S, N, and O).

Hydrated electrons (e^-_{aq}). The hydrated electron undergoes the following types of reactions: (i) reduction, (ii) dissociative electron attachment, (iii) addition to functional groups of high electron affinity, (iv) addition to aromatic rings containing electron-withdrawing substituents, and (v) addition to conjugated double bonds [45]. The hydrated electron acts as a nucleophile in its reaction with organic molecules. Similarly, as for $^\bullet$OH radicals, the rate constants for thousands of reactions of e^-_{aq} have been compiled, including reactions with molecules, ions, and radicals derived from inorganic and organic solutes [46].

Since the hydrated electron is the most powerful one-electron reductant, it is capable of reducing metal ions (Eqs. (43a)-(43c)) and inorganic anions (Eqs. (44a) and (44b)) [4, 53]:

$$e^-_{aq} + Me^+ \rightarrow Me^0 \qquad (43a)$$
$$Me^+ = Ag^+, Cu^+, Tl^+$$

$$e^-_{aq} + Me^{2+} \rightarrow Me^+ \qquad (43b)$$
$$Me^{2+} = Cu^{2+}, Co^{2+}, Cd^{2+}, Sn^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}$$

$$e^-_{aq} + Me^{3+} \rightarrow Me^{2+} \qquad (43c)$$
$$Me^{3+} = Fe^{3+}, Eu^{3+}$$

$$e^-_{aq} + MnO_4^- \rightarrow MnO_4^{2-} \qquad (44a)$$
$$e^-_{aq} + CrO_4^{2-} \rightarrow CrO_4^{3-} \qquad (44b)$$

Hydrated electrons react with many organic compounds containing substituent halogen atoms by a dissociative electron attachment (Eqs. (45a) and (45b)):

$$e^-_{aq} + RX \rightarrow R^\bullet + X^- \qquad (45a)$$
$$X = Cl, Br, I$$

$$e^-_{aq} + \text{(5-bromouracil)} \rightarrow \text{(uracil radical)} + Br^- \qquad (45b)$$

Hydrated electrons react at diffusion-controlled rates with a large number of compounds containing functional groups of high electron affinity like car-

bonyl, nitro and cyano groups (Eqs. (46a)-(46c)) by forming the corresponding radical anions [46]:

$$e^-_{aq} + >C=O \rightarrow >C^\bullet-O^- \tag{46a}$$
$$e^-_{aq} + -NO_2 \rightarrow -N^\bullet(=O)-O^- \tag{46b}$$
$$e^-_{aq} + -C\equiv N \rightarrow -C^\bullet=N^- \tag{46c}$$
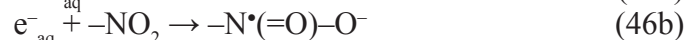
Hydrated electrons do not react with benzene with appreciable rate (k ~ 10^7 dm$^3 \cdot$mol$^{-1} \cdot$s^{-1}). However, the rate constants with benzene containing electron-withdrawing substituents (–NO$_2$, –CN) are at a diffusion-controlled limit. The resulting radical anions undergo a very rapid protonation by water (Eq. (47)), yielding the same species as expected for the addition reaction of $^\bullet$H atoms (*vide infra*) (Eq. (52)):
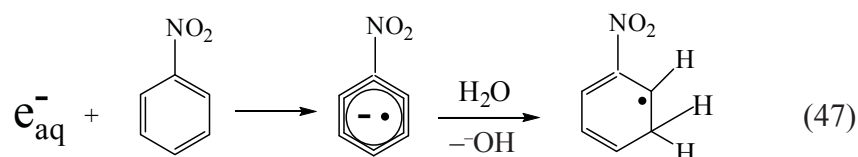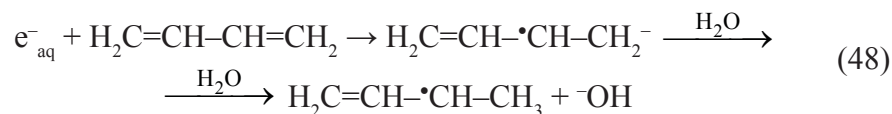

$$\tag{47}$$

Hydrated electrons are not reactive with ethylene (k < 3 × 10^5 dm$^3 \cdot$mol$^{-1} \cdot$s^{-1}). However, their reactivity substantially increase with the molecules containing conjugated double (Eq. (48)) amounts to 8 × 10^9 dm$^3 \cdot$mol$^{-1} \cdot$s^{-1}.

$$e^-_{aq} + H_2C=CH-CH=CH_2 \rightarrow H_2C=CH-{}^\bullet CH-CH_2{}^- \xrightarrow{H_2O}$$
$$\xrightarrow{H_2O} H_2C=CH-{}^\bullet CH-CH_3 + {}^-OH \tag{48}$$

$^\bullet$*H atoms*. The $^\bullet$H atom undergoes the following types of reactions: (i) electron transfer (ET), (ii) hydrogen atom abstraction, (iii) addition to C=C bonds, (iv) addition to aromatic rings, (v) addition to electron-rich functional groups, and (vi) homolytic substitution [18, 45, 46]. These reactions reflect *inter alia* its weak nucleophilic [61], and strong reducing properties, however, less than e^-_{aq}. Interestingly, radical reactions of $^\bullet$H atoms resemble those involving $^\bullet$OH radicals.

In ET reactions $^\bullet$H atoms readily reduce metal ions having lower reduction potentials (Eqs. (49a) and (49b)) and inorganic anions (Eq. (50)) [46]:

$$H + Me^+ \rightarrow H^+ + Me^0 \tag{49a}$$
$$Me^+ = Ag^+, Tl^+$$
$$H + Me^{2+} \rightarrow H^+ + Me^+ \tag{49b}$$
$$Me^{2+} = Cu^{2+}, Hg^{2+}$$
$$H + Fe(CN)_6^{3-} \rightarrow H^+ + Fe(CN)_6^{4-} \tag{50}$$

$^\bullet$H atoms also abstract hydrogen atoms, but with much lower rate constants than $^\bullet$OH radicals (Table 4). Since the H–H bond dissociation energy (104.3 kcal·mol^{-1}) is substantially lower than the BDE of H–OH bond (*vide supra*).

This phenomenon is particularly reflected in the reactions of $^\bullet$H atoms with methanol (Eq. (51)) and 2-methyl-2-propanol (*tert*-butanol) (Eq. (52))

Table 4. Comparison of the rate constants of the H-abstraction reactions involving $^\bullet$H atoms and $^\bullet$OH radicals with selected alkyl alcohols [46].

Alcohol	k ($^\bullet$H + ROH) [dm$^3\cdot$mol$^{-1}\cdot$s^{-1}]	k ($^\bullet$OH + ROH) [dm$^3\cdot$mol$^{-1}\cdot$s^{-1}]
CH_3OH	2.6×10^6	9.7×10^8
C_2H_5OH	1.7×10^7	1.9×10^9
C_3H_7OH	2.4×10^7	2.8×10^9
$(CH_3)_2CHOH$	7.4×10^7	1.9×10^9
$(CH_3)_3COH$	$(1.7\text{-}11.5) \times 10^5$	6.0×10^8

(Table 4) where the BDEs of primary hydrogens (H–CH$_2$) are only slightly lower than BDE of the H–H bond:

$$^\bullet H + CH_3OH \rightarrow H_2 + {}^\bullet CH_2OH \tag{51}$$
$$^\bullet H + (CH_3)_3C\text{–}OH \rightarrow H_2 + {}^\bullet CH_2(CH_3)_2C\text{–}OH \tag{52}$$

Addition of $^\bullet$H atoms to C=C double bonds (Eq. (53)) is very fast and occurs close to the diffusion-controlled rate (*e.g.* for ethylene $k_{53} = 3.0 \times 10^9$ dm$^3\cdot$mol$^{-1}\cdot$s^{-1}) [46]:

$$^\bullet H + H_2C{=}CH_2 \rightarrow {}^\bullet CH_2\text{–}CH_3 \tag{53}$$

Addition of $^\bullet$H atoms to aromatic rings leads directly (contrary to the $^\bullet$OH addition) to a σ-complex in which the $^\bullet$H atom bounds tightly to the carbon atoms (Eq. (54)).

$$\tag{54}$$
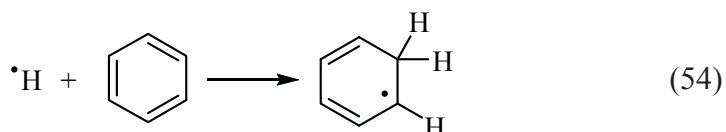
Because of the pronounced electrophilicity, $^\bullet$H atoms react readily by addition to the sulfur atoms in trithianes which contain three electron-rich thioether groups. However, the resulting adducts cannot be detected since they decompose by ring opening followed either by α- or β-scission [66].

$^\bullet$H atoms can also undergo bimolecular homolytic substitution (S$_H$2) with α-(alkylthio)carbonyl compounds (Eq. (55)) which is driven by the formation of the stronger S–H bond while simultaneously a relatively C–S bond is broken [67]:

$$^\bullet H + CH_3SCH_2C({=}O)NH_2 \rightarrow CH_3SH + {}^\bullet CH_2C({=}O)NH_2 \tag{55}$$

Radical reactions involving primary radicals from water radiolysis have been successfully used for the generation, identification and spectral and kinetic characterization of a large variety of radicals and radical ions derived from biological molecules, like amino acids, peptides, proteins, DNA and its constituents, and lipids. Numerous books and review articles addressing these topics have been published [11, 15, 45, 68-73].

2.1.5. Radical reactions involving $O_2^{\bullet-}$ and $HO_2^{\bullet}$ radicals

In principle, the reactivity of $O_2^{\bullet-}$ and $HO_2^{\bullet}$ radicals with organic compounds in aqueous solutions is rather low [57]. For instance, the reactions of $HO_2^{\bullet}/O_2^{\bullet-}$ with amino acids in their zwitterionic forms were found to be very slow with the rate constants in the range of 10^1-10^2 $dm^3 \cdot mol^{-1} \cdot s^{-1}$ [74]. The reactivity of $O_2^{\bullet-}$ and $HO_2^{\bullet}$ radicals with some biologically relevant compounds including metal ions and metal ion complexes have been studied extensively. Some selected rate constants are listed in Table 5.

Table 5. Comparison of the rate constants of $O_2^{\bullet-}$ and $HO_2^{\bullet}$ radicals with some selected metal ions, metal ion complexes, and organic compounds [74].

Compound (S)	k $(O_2^{\bullet-}$ + S) $[dm^3 \cdot mol^{-1} \cdot s^{-1}]$	k $(HO_2^{\bullet}$ + S) $[dm^3 \cdot mol^{-1} \cdot s^{-1}]$
Ascorbic acid (AH)	n.m.	1.6×10^4
Ascorbate anion (AH$^-$)	2.6×10^8	5.0×10^9
Nicotinamide-adenine dinucleotide – NADH	< 27	1.8×10^5
Fe^{II}	1.0×10^7	1.2×10^6
Fe^{III}	1.5×10^8	$< 10^3$
Cu^{II}	1.0×10^{10}	1.0×10^9
Cu^{I}	$(5\text{-}8) \times 10^9$	1.0×10^6
Mn^{II} porphyrins	5.6×10^8-9.0×10^9	–
Mn^{III} porphyrins	4.0×10^5-5.1×10^7	–
Fe^{II} porphyrins	3.1×10^6-3.7×10^8	–
Fe^{III} porphyrins	3.0×10^5-2.0×10^9	–

A majority of research has focused on iron, copper, manganese and their complexes. These metal ions are present in the active sites of superoxide dismutases.

2.1.6. Selective secondary radicals: generation, spectral, kinetic, and redox properties

Since the $^{\bullet}OH$ radical is a very strong oxidant and both e^-_{aq} and $^{\bullet}H$ atoms are very strong reductants, they do not react in a selective way. They react very fast with almost all compounds in various types of reactions. Moreover, in one-electron oxidation reactions $^{\bullet}OH$ radicals react with formation of a primary intermediate adduct which subsequently, in some cases, is transformed to one-electron oxidized products. Thus, there was a strong need for a generation of more selective radicals that are less reactive and/or can react mostly by a direct electron transfer [1, 4, 18].

Selective oxidizing radicals. A large variety of oxidizing inorganic radicals have been generated and their spectra, reaction rate constants with numerous substrates, and reduction potentials have been measured and compiled [48].

Selected examples of reactions leading to generation of the oxidizing selective inorganic radicals (using primary $^\bullet OH$ radicals) are presented below (Eqs. (56a)-(56d)):

$$^\bullet OH + X^- \rightarrow XOH^{\bullet-} \leftrightarrows {}^-OH + X^\bullet \xrightleftharpoons{X^-} X_2^{\bullet-} \qquad (56a)$$
$$X^- = Cl^-, Br^-, I^-, SCN^-$$

$$^\bullet OH + N_3^- \rightarrow {}^-OH + N_3^\bullet \xrightleftharpoons{N_3^-} N_6^{\bullet-} \qquad (56b)$$

$$^\bullet OH + X^- \rightarrow {}^-OH + X^\bullet \qquad (56c)$$
$$X^- = ClO_2^-, NO_2^-$$
$$^\bullet OH + X^{2-} \rightarrow {}^-OH + X^{\bullet-} \qquad (56d)$$
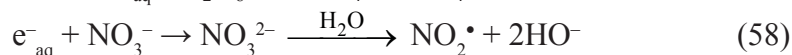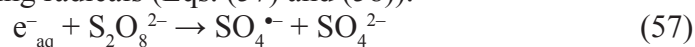$$X^{2-} = CO_3^{2-}, SO_3^{2-}, SeO_3^{2-}$$
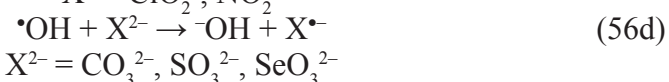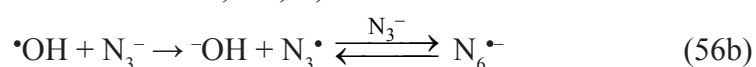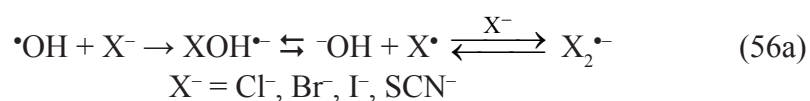
A compilation of some spectral parameters and reduction potentials of the most common oxidizing and reductive inorganic radicals is presented in Table 6.

Table 6. Spectral parameters and reduction potentials of some selective inorganic radicals [49, 53].

Radical	λ_{max} [nm] [49]	ε [dm$^3\cdot$mol$^1\cdot$cm^{-1}] [49]	Redox couple [53]	E^0 *vs.* NHE [V] [53]
$SO_4^{\bullet-}$	450	1100	$SO_4^{\bullet-}/SO_4^{2-}$	+2.47
$Cl_2^{\bullet-}$	340	8800	$Cl_2^{\bullet-}/2Cl^-$	+2.30
$NO_3^\bullet$	640	800-1000	$NO_3^\bullet/NO_3^-$	+2.3-2.5
$CO_3^{\bullet-}$	600	1860	$CO_3^{\bullet-}/CO_3^{2-}$	+1.78
$SeO_3^{\bullet-}$	420	1470	$SeO_3^{\bullet-}/SeO_3^{2-}$	+1.68
$Br_2^{\bullet-}$	360	9900	$Br_2^{\bullet-}/2Br^-$	+1.66
$(SCN)_2^{\bullet-}$	472	7580	$(SCN)_2^{\bullet-}/2SCN^{\bullet-}$	+1.33
$N_3^\bullet$	274	2025	$N_3^\bullet/N_3^-$	+1.33
$I_2^{\bullet-}$	380	9400	$I_2^{\bullet-}/2I^-$	+1.04
$NO_2^\bullet$	400	200	$NO_2^\bullet/NO_2^-$	+0.99
$ClO_2^\bullet$	360	1000	$ClO_2^\bullet/ClO_2^-$	+0.93
$SO_3^{\bullet-}$	250-255	1000-1380	$SO_3^{\bullet-}/SO_3^{2-}$	+0.63
$NO^\bullet$	–	–	$NO^\bullet/NO^-$	+0.39
$SO_2^{\bullet-}$	255	1770	$SO_2/SO_2^{\bullet-}$	−0.28
$CO_2^{\bullet-}$	235	3000	$CO_2/CO_2^{\bullet-}$	−1.90

Reactions involving hydrated electrons are also very useful for the generation of selective oxidizing radicals (Eqs. (57) and (58)):

$$e^-_{aq} + S_2O_8{}^{2-} \rightarrow SO_4{}^{\bullet-} + SO_4{}^{2-} \tag{57}$$

$$e^-_{aq} + NO_3{}^- \rightarrow NO_3{}^{2-} \xrightarrow{H_2O} NO_2{}^\bullet + 2HO^- \tag{58}$$

Selective reductive radicals. The number of selective reductive radicals is much lower in comparison to oxidizing radicals. The most common is the carbon dioxide radical anion ($CO_2{}^{\bullet-}$). Reactions leading to this radical and involving primary $^\bullet OH$ radicals and $^\bullet H$ atoms are presented below (Eqs. (59) and (60)):

$$^\bullet OH + HCO_2{}^- \rightarrow H_2O + CO_2{}^{\bullet-} \tag{59}$$

$$^\bullet H + HCO_2{}^- \rightarrow H_2 + CO_2{}^{\bullet-} \tag{60}$$
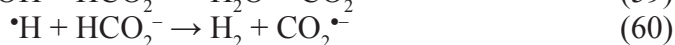
These secondary radicals exhibit sufficiently intense optical absorption in the visible and near UV range that permit kinetic spectrophotometric measurements of the rates of their formation and decay.

2.1.7. Radical reactions involving secondary radicals

Selective inorganic radicals react with other radicals and with inorganic and organic compounds mostly by one-electron oxidation or reduction without the formation of intermediate adducts (such as $^\bullet OH$ and $^\bullet H$ adducts). A comparison of the reactivities of some selected oxidizing radicals with inorganic and organic compounds is presented in Table 7.

Table 7. Rate constants k of some selected oxidizing radicals with inorganic and organic compounds [48].

Compound	k [dm$^3\cdot$mol$^{-1}\cdot$s^{-1}]					
	$SO_4{}^{\bullet-}$	$Cl_2{}^{\bullet-}$	$CO_3{}^{\bullet-}$	$Br_2{}^{\bullet-}$	$N_3{}^\bullet$	$I_2{}^{\bullet-}$
$N_3{}^-$	3.0×10^9	1.2×10^9	–	4.0×10^8	–	$< 5 \times 10^6$
$Fe(CN)_6{}^{2-}$	–	–	2.7×10^8	2.8×10^7	4.0×10^9	–
Benzene	–	–	$< 5 \times 10^4$	–	$< 3 \times 10^6$	–
Anisole	4.9×10^9	–	2.8×10^5	–	$< 3 \times 10^6$	–
Phenol	–	4.0×10^8	2.0×10^7	6.0×10^6	5.0×10^7	–
Phenoxide	–	–	3.5×10^8	5.0×10^8	4.3×10^9	5.7×10^7
4-Methoxy-phenoxide	–	–	5.2×10^8	–	4.2×10^9	–
4-Methyl-phenoxide	–	–	4.8×10^8	4.7×10^8	–	9.8×10^7
Aniline	–	–	5.4×10^8	2.1×10^8	4.0×10^9	4.4×10^6
Tryptophan	2.0×10^9	2.6×10^9	4.4×10^8	7.0×10^8	4.1×10^9	$< 1 \times 10^6$
Tyrosine	3.0×10^9	2.7×10^8	2.1×10^8	2.0×10^8	1.0×10^8	$< 1 \times 10^6$
Methionine	1.1×10^9	4.0×10^9	3.0×10^7	1.7×10^9	$< 1 \times 10^6$	$< 1 \times 10^6$

For instance, the azide radical ($N_3^\bullet$) was found to oxidize aromatic systems such as aniline and phenoxide ions at a rate $\sim 4 \times 10^9$ dm$^3\cdot$mol$^{-1}\cdot$s^{-1}, primarily *via* ET, whereas benzene and anisole are not observably oxidized by $N_3^\bullet$. Some of the presented radicals ($Cl_2^{\bullet-}$, $CO_3^{\bullet-}$, $N_3^\bullet$, and $Br_2^{\bullet-}$) show a great selectivity for tryptophan (Trp) residues in the presence of tyrosine (Tyr) residues. Moreover, these radicals react quite rapidly with amino acid residues (Trp, Tyr, Met, Cys, His) forming respective radicals located mostly on their side chains. These radicals are particularly useful for studying oxidative changes in amino acids, peptides and proteins that were very often coupled with long-range intramolecular electron transfer (LRET) [75-80].

2.1.8. Peroxyl radicals

Peroxyl radicals (ROO$^\bullet$) are important reactive intermediates formed during oxidation of organic and biological compounds which result from the reaction of free radical (R$^\bullet$) with molecular oxygen (Eq. (61)):

$$RX^\bullet + O_2 \rightarrow RXO_2^\bullet \tag{61}$$
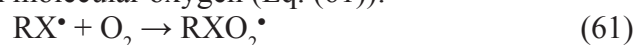
The radical site (-X$^\bullet$) is mostly located on non-metallic elements like carbon, oxygen, nitrogen and sulfur atoms. The most common peroxyl radicals are those involving carbon atom. These radicals are key intermediates in polymerization processes, either in a chain propagation step and/or termination step. Formation and reactions of ROO$^\bullet$ radicals have been extensively reviewed in numerous publications [81-84].

Carbon-atom peroxyl radicals. Most organic C-centered radicals react, in principle, irreversibly with O$_2$ with the rate constants typically $\sim 2 \times 10^9$ dm$^3\cdot$mol$^{-1}\cdot$s^{-1} [85]. As far as the spectral properties are concerned the case frequently encountered is that the parent C-centered radical absorbs in the UV-Vis region while the corresponding peroxyl radical absorbs weakly only in the UV region with no specific spectral structure. The other case, where both the radical and its

Table 8. Absorption maxima and molar absorption coefficients of some selected vinyl peroxyl and aryl peroxyl radicals in aqueous solutions [81].

Peroxyl radical	λ_{max} [nm]	ε_{max} [dm$^3\cdot$mol$^{-1}\cdot$cm^{-1}]
Vinyl	440	1100
Dichlorovinyl	540	1100
Phenyl	490	1600
4-Methoxyphenyl	600	2100
4-Methylphenyl	560	600
4-Aminophenyl	590	2000
3-Hydroxyphenyl	520	1400

corresponding peroxyl radical absorb in the UV region has been also observed. Usually, those peroxyl radicals are characterized by weak absorptions with λ_{max} < 250 nm and rather low molar absorption coefficients ~1000 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$. Interestingly, the situation in the case of vinyl and aryl radicals is the inverse. The parent radicals exhibit no absorption in the accessible wavelength region while their respective peroxyl radicals absorb in the near UV or even in the visible region. Some selected examples are compiled in Table 8.

Peroxyl radicals can undergo a number of unimolecular and bimolecular processes. Unimolecular processes include following types of reactions: $HO_2^\bullet$ and $O_2^{\bullet-}$ elimination reactions, addition to the C=C double bonds, and, the most common, hydrogen abstraction and electron transfer reactions. Since the ROO–H bond energy in hydroperoxides derived from $ROO^\bullet$ radicals is rather weak (~360-370 $kJ \cdot mol^{-1}$), the H-abstraction reaction can occur at an appreciable rate, since the C–H bond energy of the H-donor is sufficiently low. Such conditions are fulfilled in abstraction of bis-allylic hydrogens present in polyunsaturated fatty acids where the C–H bond energy is equal to 320 $kJ \cdot mol^{-1}$ (Eq. (62)) [81, 86]:

$$ROO^\bullet + -CH_2=CH-CH_2-CH=CH- \rightarrow$$
$$\rightarrow ROOH + -CH_2=CH-^\bullet CH-CH=CH- \quad (62)$$
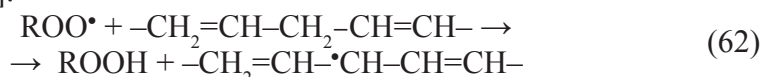
Peroxyl radicals can oxidize various organic compounds (phenothiazines, porphyrins, amines, sulfides) to the corresponding radical cations and various anions (ascorbate, phenolate, inorganic anions) to the corresponding radicals [85, 86]. N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD) was used to probe the oxidizing properties of various peroxyl radicals. The rate constants of peroxyl radicals cover a broad range from 1.1 × 10^6 $dm^3 \cdot mol^{-1} \cdot s^{-1}$ to 1.9 × 10^9 $dm^3 \cdot mol^{-1} \cdot s^{-1}$ (Table 9).

Table 9. Rate constants k of some selected peroxyl radicals with ascorbate anions and TMPD [86].

	k [$dm^3 \cdot mol^{-1} \cdot s^{-1}$]				
	$CH_3O_2^\bullet$	$HOCH_2O_2^\bullet$	$ClCH_2O_2^\bullet$	$Cl_2CHO_2^\bullet$	$Cl_3CO_2^\bullet$
Ascorbate (AH⁻)	1.7 × 10^6	4.7 × 10^6	1.2 × 10^8	7.0 × 10^8	9.1 × 10^8
TMPD	4.3 × 10^7	7.2 × 10^7	4.2 × 10^8	7.4 × 10^8	1.7 × 10^9

It is worthy to note that the rate constants for oxidation reactions by peroxyl radicals increase with increasing number of chlorine atoms on the radicals. This trend was rationalized by the electron-withdrawing effect of these substituents which decrease the electron density on the radical site.

Peroxyl radicals, which do not decay in one of the unimolecular processes (*vide supra*), undergo bimolecular decay. In contrast to many other radicals,

they do not disproportionate but decay *via* a recombination process leading in the first step to a tetroxide (Eq. (63)):

$$ROO^\bullet + ROO^\bullet \rightarrow ROOOOR \tag{63}$$

Depending on the properties of the peroxyl radicals, the tetroxide can decay *via* several channels (Eqs. (64) and (65)), which always involve the cleavage of the lateral O–O bond. Reactions depicted in Eqs. (64) and (65) are known as the Russell and the Bennett mechanisms, respectively:

$$ROOOOR \rightarrow R_2C{=}O + R_2CHOH + O_2 \tag{64}$$
$$ROOOOR \rightarrow 2R_2C{=}O + H_2O_2 \tag{65}$$

These reaction pathways require the existence of C–H bond α-positioned to the peroxyl function.

Hetero-atom peroxyl radicals. Oxygen-centered radicals react with O_2 very slowly, *e.g.* the tyrosyl radical (TyrO$^\bullet$) reacts with O_2 with the rate $< 1.3 \times 10^3$ dm$^3 \cdot$mol$^{-1} \cdot$s^{-1}. In principle, trioxyl radicals ROOO$^\bullet$ are unstable and decompose into alkoxyl radicals (RO$^\bullet$) and O_2.

Nitrogen-centered radicals react with O_2 more slowly than C-centered radicals. For instance, the rate constant for the reaction of aminyl radical ($^\bullet$NH$_2$) with oxygen was found to be equal to 3.4×10^7 dm$^3 \cdot$mol$^{-1} \cdot$s^{-1}.

Sulfur-centered radicals react with oxygen fast and the reverse reaction is also fast (Eq. (66)):

$$RS^\bullet + O_2 \leftrightarrows RSOO^\bullet \tag{66}$$

For the thiyl radical derived from mercaptoethanol (CH$_3$CH$_2$S$^\bullet$) the reaction with O_2 is diffusion controlled with $k_{66} = 2.2 \times 10^9$ dm$^3 \cdot$mol$^{-1} \cdot$s^{-1} while the reverse reaction $k_{-66} = 6.2 \times 10^5$ s^{-1} implies the existence of equilibrium depicted in Eq. (66) [87, 88]. Thiyl peroxyl radicals can be monitored by UV-Vis spectroscopy due to their absorption band with λ_{max} located at 550 nm despite their low molar absorption coefficient $\varepsilon_{550} = (2\text{-}4) \times 10^2$ dm$^3 \cdot$mol$^{-1} \cdot$cm^{-1}. Thiyl peroxyl radicals undergo a thermal rearrangement to the thermodynamically more stable sulfonyl radicals (Eq. (67)), which can be further oxidized to sulfonyl peroxyl radicals (Eq. (68)):

$$RSOO^\bullet \rightarrow RS^\bullet({=}O)_2 \tag{67}$$
$$RS^\bullet({=}O)_2 \rightarrow RS\,({=}O)_2{-}OO^\bullet \tag{68}$$
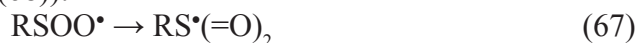
These intermediates have attracted considerable interest because of their possible participation in radical processes occurring in biological systems.

2.2. RADIOLYSIS OF WATER AT AMBIENT TEMPERATURES WITH HIGH LET IRRADIATION

The earliest studies on radiolysis of water with high LET irradiation were performed just after discovery of radiation. However, only α-particles were available at that time. Later, the development of ion accelerators has enabled studies with ions (H$^+$, D$^+$, He^{2+}) of lower energies (10 MeV per ion-mass num-

ber). In the last two decades of twentieth century, ion beams of heavier ions with higher energies have become available. Facilities in France (GANIL), Japan (TIARA), Germany (FAIR), and in USA (NSRL) delivered C-Kr ions with 75-95 MeV/ion-mass number, H-Au ions with 2.5-27 MeV/ion-mass number, H-U ions with 2-10 GeV/ion-mass number, and Ne-Au with 0.3-1.5 GeV/ion-mass number, respectively [89].

2.2.1. Primary yields of $^\bullet$OH radicals, e^-_{aq}, and H_2O_2 as a function of LET [89-92]

The most intensively studied products of water radiolysis were hydrated electrons (e^-_{aq}), $^\bullet$OH radicals, and hydrogen peroxide (H_2O_2). Many of the results were obtained by a scavenging method [42]. Some of them were from the heavy-ion pulse radiolysis.

Hydrated electrons and $^\bullet$OH radicals. There are two important findings as far as the primary G-values are concerned: (i) the primary yields of e^-_{aq} and $^\bullet$OH radicals decrease with increasing LET (Table 10), and (ii) the lower primary yields of e^-_{aq} and $^\bullet$OH radicals are observed for lighter ions than for heavier ions with comparable LET.

Hydrogen peroxide. As compared to $^\bullet$OH radicals, e^-_{aq}, the radiation chemical yields are less sensitive to variation of LET (see Table 7).

Based on the dependency of G-values of the above products *vs.* LET (Table 10) the three reactions depicted by Eqs. (10), (11) and (15) of Table 1 seem to be the most significant among all intra-spur and intra-track reactions.

Table 10. Primary radiation chemical yields (per 100 eV) of e^-_{aq}, $^\bullet$OH radicals, and H_2O_2 as a function of LET.

	Species/ions				Species/ions		
	e^-_{aq}	$^\bullet$OH	H_2O_2		e^-_{aq}	$^\bullet$OH	H_2O_2
He ($\sim$2 eV·nm^{-1})	2.4	2.6	0.7	Si ($\sim$60 eV·nm^{-1})	1.2	1.3	0.75
C ($\sim$15 eV·nm^{-1})	1.9	1.9	0.8	Ar ($\sim$150 eV·nm^{-1})	1.1	1.1	0.9
Ne ($\sim$30 eV·nm^{-1})	1.6	1.6	0.8	Fe ($\sim$600 eV·nm^{-1})	0.8	1.0	1.1

2.2.2. Intra-track radical kinetics as a function of LET [93]

Information about the intra-track dynamics can be extracted by increasing scavenger concentration. With increasing scavenger concentration, the scavenging reactions become more efficient, and thus they can compete more significantly with intra-track reactions and diffusions.

The following chemical system was applied to the study the intra-track radical kinetics induced by different high LET irradiation: a deaerated aqueous

solutions containing methyl viologen (MV^{2+}) containing various concentration of formate ions ($HCOO^-$). The following reactions occur (Eqs. (18), (69)-(72)):

$$e^-_{aq} + MV^{2+} \rightarrow MV^{\bullet+} \quad\quad\quad (69)$$
$$^\bullet OH + HCOO^- \rightarrow H_2O + CO_2^{\bullet-} \quad\quad\quad (70)$$
$$^\bullet H + HCOO^- \rightarrow H_2 + CO_2^{\bullet-} \quad\quad\quad (71)$$
$$CO_2^{\bullet-} + MV^{2+} \rightarrow CO_2 + MV^{\bullet+} \quad\quad\quad (72)$$
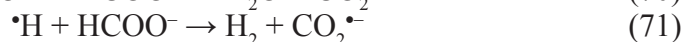
The G-values of $MV^{\bullet+}$ were measured in aqueous solutions after irradiation with He, C, Ne, Si, Ar, and Fe ions. The $G(MeV^{\bullet+})$ increased with increasing $HCOO^-$ concentration for all ions. This is due to the faster scavenging reactions in which more primary radicals are scavenged. With increasing LET, the $G(MeV^{\bullet+})$ decreased due to increased radical density in the track and as a consequence of increased efficiency of intra-track reactions. These experimental data were successfully reproduced by the Monte-Carlo simulation using the IONLYS-IRT code.

3. RADIOLYSIS OF ORGANIC SOLVENTS

There is a large variety of organic solvents that have been used for inducing radical reactions by means of high energy radiation [94]. The use of organic solvents has advantages over water. First, since a broad range of solvent polarities are available, compounds that are insoluble in water can be studied in a suitable solvent or mixture of solvents [4]. Second, depending on the solvent used, its radiolysis can offer a convenient method for the generation of radical ions and excited states and/or preferentially one of them. Some control over the type of ionic species and excited states formed can be achieved by choice of a suitable solvent and, in addition, of a saturating gas [5]. Thus, one may generate selectively radical cations, radical anions, and/or excited states derived from the solutes. The one disadvantage is the lack of a detailed knowledge of the mechanism of secondary processes occurring after primary ionization and/or excitation of some solvents. In contrast to water, there are still discrepancies as to the type and radiation chemical yields of primary radiolysis products. Product and free ion yields, rate constants, and spectroscopic parameters of transients in selected organic liquids have been collected [95-97].

Only the radiolysis of some most representative solvents (alcohols, acetonitrile, acetone, and halogenated hydrocarbons) for the generation of radical ions and excited states are covered here.

3.1. RADIOLYSIS OF ALCOHOLS

### 3.1.1. Formation of primary transients and their subsequent reactions

Radiolysis of neat alcohols leads to the formation of the alcohol positive ions and presolvated electrons ($e^-_{presolv}$) (Eq. (73)) [98, 99]:

$$RR'CH–OH \text{ -}{\wedge\wedge\wedge\wedge\wedge}{\rightarrow} RR'CH–OH^{\bullet+} + e^-_{presolv} \qquad (73)$$
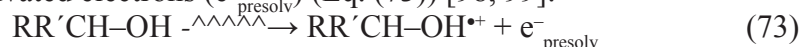
The alcohol derived radical cations disappear rapidly in ion-molecule reactions with another alcohol molecule producing either ketyl radicals (Eq. (74a)) or alkoxy radicals (Eq. (74b)):

$$\rightarrow RR'C^{\bullet}–OH + RR'CH–OH_2^+ \qquad (74a)$$

$$RR'CH–OH^{\bullet+} + RR'CH–OH\ |$$

$$\rightarrow RR'CH–O^{\bullet} + RR'CH–OH_2^+ \qquad (74b)$$

The reaction depicted in Eq. (74a) prevails substantially over the reaction depicted in Eq. (74b) since the >C–H bond dissociation energy (95 kcal·mol^{-1}) is lower than the BDE of the O–H bond (102 kcal·mol^{-1}). Similarly, as in water, the electron ejected in an ionization process (Eq. (73)), undergoing solvation on the picosecond time domain, after thermalization (Eq. (75)):

$$e^-_{presolv} + nRR'CH–OH \rightarrow e^-_{solv} \qquad (75)$$
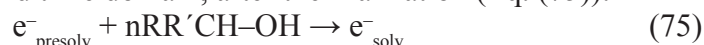
When the alcohol solutions are saturated with nitrous oxide (N_2O), the reduction reactions involving only ketyl radicals can be studied without a contribution of solvated electrons (e^-_{solv}). Solvated electrons can be rapidly scavenged by N_2O generating oxide radical ions ($O^{\bullet-}$) (Eq. (76)), which subsequently react with alcohol molecules forming ketyl radicals (Eq. (77)):

$$e^-_{solv} + N_2O \rightarrow N_2 + O^{\bullet-} \qquad (76)$$

$$O^{\bullet-} + RR'CH–OH \rightarrow {}^-OH + RR'C^{\bullet}–OH \qquad (77)$$
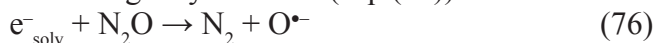
Since in alcohols mainly solvated electrons and reductive ketyl radicals ($RR'C^{\bullet}–OH$) are formed (Eqs. (73), (74a) and (77)), these solvents can be used to generate selectively radical anions derived from the solutes, as described below.

3.1.2. Selected radical reactions involving primary transients

A few systems will be presented to illustrate the generation of solute radical anions *via* reactions of e^-_{solv} and ketyl radicals with solute molecules and subsequent reactions of radical anions in alcohol solutions. Solute radical cations are not formed since the alcohol-derived radical cations disappear rapidly in reactions depicted in Eqs. (74a) and (74b).

Radical anions derived from retinyl polyene derivatives (Ret), retinal homologs (HomRet) and carotenes (Car) have been studied in methanol and 2-propanol [100, 101]:

$$Ret/HomRet/Car + e^-_{solv}/RR'C^{\bullet}–OH \rightarrow$$

$$\rightarrow Ret^{\bullet-}/HomRet^{\bullet-}/Car^{\bullet-} + RR'C{=}O + H^+ \qquad (78)$$

Radical anions derived from Ret and HomRet formed in reactions (Eq. (78)) undergo protonation by alcohol molecules (Eq. (79)) [102]:

$$\text{Ret}^{\bullet-}/\text{HomRet}^{\bullet-} + \text{RR'CH–OH} \rightarrow \text{RetH}^{\bullet}/\text{HomRet}^{\bullet} + \text{RR'CH–O}^- \quad (79)$$

The rate constants for protonation of radical anions in alcohols was found to decrease on increasing the polyene chain and the acidity of the hydroxyl group in alcohols.

Radical anions derived from fullerenes (C_{60}, $C_{70,}$ C_{76}, C_{78}, and C_{84}) have been generated (in analogous reactions as depicted by Eq. (78)) and their spectral and kinetic properties have been characterized in 2-propanol [103].

Radical anions derived from naphthalene ($\text{Nph}^{\bullet-}$), phenanthrene ($\text{Pha}^{\bullet-}$), biphenyl ($\text{Bph}^{\bullet-}$), anthracene ($\text{Anh}^{\bullet-}$), *p-, o-, m*-terphenyls ($t\text{-Phe}^{\bullet-}$) undergo protonation in analogous reactions as depicted by Eq. (79).
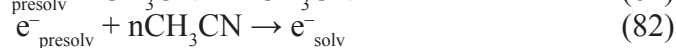
3.2. RADIOLYSIS OF ACETONITRILE

3.2.1. Formation of primary transients and their subsequent reactions

Radiolysis of neat acetonitrile leads to the formation of acetonitrile positive radical ions and presolvated electrons (Eq. (80)):

$$\text{CH}_3\text{CN} \text{ -}\wedge\wedge\wedge\wedge\wedge\rightarrow \text{CH}_3\text{CN}^{\bullet+} + e^-_{presolv} \quad (80)$$
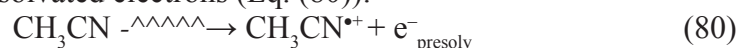
Presolvated electrons are mostly efficiently scavenged by the acetonitrile molecules leading to the formation of negative ions (Eq. (81)) or, to a lower extent, undergo solvation (Eq. (82)) and are subsequently trapped by the acetonitrile molecules (Eq. (83)):
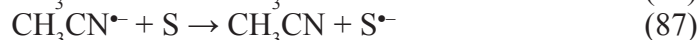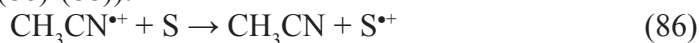
$$e^-_{presolv} + \text{CH}_3\text{CN}^- \rightarrow \text{CH}_3\text{CN}^{\bullet-} \quad (81)$$
$$e^-_{presolv} + n\text{CH}_3\text{CN} \rightarrow e^-_{solv} \quad (82)$$
$$e^-_{solv} + \text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CN}^{\bullet-} \quad (83)$$

Recombination of positive radical ions with solvated electrons (Eq. (84)) and negative radical ions (Eq. (85)) leads to the excited triplet states:

$$\text{CH}_3\text{CN}^{\bullet+} + e^-_{solv} \rightarrow {}^3\text{CH}_3\text{CN}^* \quad (84)$$
$$\text{CH}_3\text{CN}^{\bullet+} + \text{CH}_3\text{CN}^{\bullet-} \rightarrow {}^3\text{CH}_3\text{CN}^* \quad (85)$$

The yields of reducing species was found in the range of G = 1.03-1.55. On the other hand, the low yields of G for the oxidizing species (~0.2) and for the triplets (~0.3) were measured [104, 105]. Contrary to alcohols, acetonitrile is an aprotic solvent which makes acetonitrile a convenient liquid system to study one-electron reduction of transition metal complexes that are not stable in aqueous and alcohol solutions and of the solute-derived radical anions which do not undergo a fast protonation by acetonitrile molecules.

3.2.2. Selected radical reactions involving primary transients

Taking into account the mechanism of radiolysis, Ar-saturated acetonitrile solutions were often used to generate of both radical cations and anions derived from the solutes (Eqs. (86)-(88)):

$$\text{CH}_3\text{CN}^{\bullet+} + \text{S} \rightarrow \text{CH}_3\text{CN} + \text{S}^{\bullet+} \quad (86)$$
$$\text{CH}_3\text{CN}^{\bullet-} + \text{S} \rightarrow \text{CH}_3\text{CN} + \text{S}^{\bullet-} \quad (87)$$

$$e^-_{solv} + S \rightarrow S^{\bullet-} \tag{88}$$

However, in O_2-saturated acetonitrile solutions, selective generation of radical cations of solute can be achieved (Eq. (86)). Oxygen serves as a strong quencher of solvated electrons, radical anions (Eq. (89)) and solvent triplets:

$$e^-_{solv}/CH_3CN^{\bullet-}/{}^3CH_3CN^* + O_2 \rightarrow O_2^{\bullet-} + CH_3CN \tag{89}$$
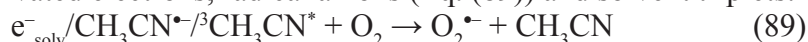
Radical ions derived from many aromatic compounds have been generated according to reactions depicted in Eqs. (86)-(88) [105-107].

3.3. RADIOLYSIS OF ACETONE

3.3.1. Formation of primary transients and their subsequent reactions

Radiolysis of neat acetone leads to the formation of the acetone positive ions and presolvated electrons (Eq. (90)):

$$(CH_3)_2 C{=}O \text{ -}^{\wedge\wedge\wedge\wedge\wedge}\rightarrow (CH_3)_2C{=}O^{\bullet+} + e^-_{presolv} \tag{90}$$

The subsequent reactions of the primarily formed species (Eq. (90)) are analogous to those occurring in acetonitrile and depicted in Eqs. (81)-(85). The total yield of excited states ($G = 1.3$) and of free ions ($G = 1.2$) were found [108].
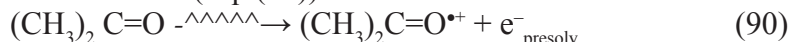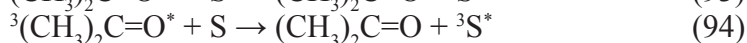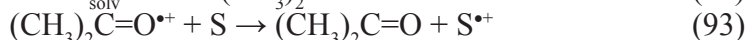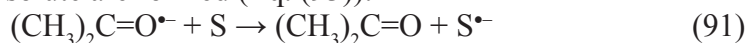
3.3.2. Selected radical reactions involving primary transients

In Ar-saturated acetone solutions both radical ions (Eqs. (91)-(93)) and triplets (Eq. (94)) of solutes are formed, while in O_2-saturated solutions, only radical cations of a solute are formed (Eq. (93)):

$$(CH_3)_2C{=}O^{\bullet-} + S \rightarrow (CH_3)_2C{=}O + S^{\bullet-} \tag{91}$$
$$e^-_{solv} + S \rightarrow (CH_3)_2C{=}O + S^{\bullet-} \tag{92}$$
$$(CH_3)_2C{=}O^{\bullet+} + S \rightarrow (CH_3)_2C{=}O + S^{\bullet+} \tag{93}$$
$${}^3(CH_3)_2C{=}O^* + S \rightarrow (CH_3)_2C{=}O + {}^3S^* \tag{94}$$
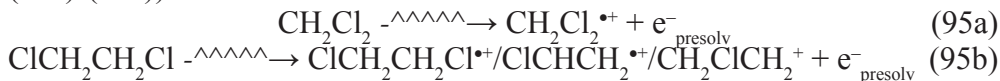
Radical ions and triplet excited states of naphthalene, anthracene, pyrene, biphenyl, *trans*-stilbene, nitromethane, retinyl polyenes derivatives, and retinal homologs have been generated *via* reactions depicted in Eqs. (90)-(94), and studied in acetone [108-110]. Radical cations of multiple methylated uracils and thymines were also generated, and were found to exist in a lactim-like form [110].

3.4. RADIOLYSIS OF HALOGENATED HYDROCARBONS

3.4.1. Formation of primary transients and their subsequent reactions

Radiolysis of neat halogenated hydrocarbons (RCl), leads to the formation of the positive radical ions and/or radicals and presolvated electrons (Eqs. (95a)-(95c)):

$$CH_2Cl_2 \text{ -}^{\wedge\wedge\wedge\wedge\wedge}\rightarrow CH_2Cl_2^{\bullet+} + e^-_{presolv} \tag{95a}$$
$$ClCH_2CH_2Cl \text{ -}^{\wedge\wedge\wedge\wedge\wedge}\rightarrow Cl\overset{\bullet}{C}H_2CH_2Cl^{\bullet+}/ClCH\overset{\bullet}{C}H_2^{\bullet+}/\overset{\bullet}{C}H_2ClCH_2^+ + e^-_{presolv} \tag{95b}$$

$$n\text{-}(C_4H_9)Cl \xrightarrow{\;\wedge\wedge\wedge\wedge\wedge\;} n\text{-}(C_4H_9)Cl^{\bullet+} + e^-_{presolv} \qquad (95c)$$
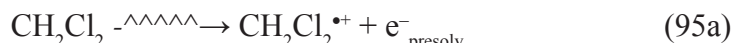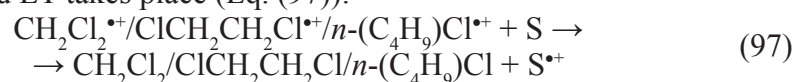
Presolvated electrons are mostly efficiently scavenged by the RCl molecules (dichloromethane, 1,2-dichloroetane, and *n*-butyl chloride) *via* a very fast dissociative attachment to the solvent molecules forming relatively unreactive radicals and chloride ions (Cl⁻) which do not react with the solute (Eq. (96)):

$$e^-_{presolv} + RCl \rightarrow R^\bullet + Cl^- \qquad (96)$$

or to lower extent undergo solvation and a subsequent trapping by the RCl molecules leading to the same products as in reaction depicted in Eq. (96) [111]. Thus, direct reactions of electrons with the solutes are eliminated and therefore these halogenated hydrocarbons are very convenient for the selective generation of solute radical cations.

3.4.2. Selected radical reactions involving primary transients

In the presence of solutes (S) of lower ionization potential as the above solvents, a rapid ET takes place (Eq. (97)):

$$CH_2Cl_2^{\bullet+}/ClCH_2CH_2Cl^{\bullet+}/n\text{-}(C_4H_9)Cl^{\bullet+} + S \rightarrow$$
$$\rightarrow CH_2Cl_2/ClCH_2CH_2Cl/n\text{-}(C_4H_9)Cl + S^{\bullet+} \qquad (97)$$

Radical cations derived from retinal and retinoic acid, fullerenes (C_{60}, C_{70}, C_{76}, C_{78}, and C_{84}) and chlorinated fullerenes ($C_{60}Cl_6$ and $C_{60}Cl_{12}$) have been generated *via* reactions depicted in Eq. (86) and their spectral properties have been characterized [103, 112, 113].

4. RADIOLYSIS OF IONIC LIQUIDS

Ionic liquids (ILs) constitute a bridge between molecular liquids and ionic solids. They are defined as molten salts with melting points below 100°C. These salts are a combination of organic and inorganic ions. The dynamic properties (*e.g.* relaxation) are distributed over a broader range of scales and diffusion is generally slower due to higher viscosities in comparison to molecular liquids. ILs are generally characterized by low volatility, good electric conductivity, and microheterogeneity producing different local environments that favors simultaneous solubility of polar and non-polar solutes [114]. Owing to their unique properties, ILs are an attractive media for the generation of radicals *via* high energy radiation. However, the knowledge about the radiation-induced primary reactive intermediates in ILs, and the approaches to convert them into specific radical intermediates is limited to only some investigated ILs. These comprise ILs composed of imidazolium ($BMIM^+$), quaternary ammonium (R_4N^+), pyrrolidinium, (Pyr), pyridinium (Py), phosphonium cations and bis(trifluoromethylsulfonyl)imide (NTf_2^-), dicyanamide, bis-(oxalate)-borate, tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), chloride (Cl⁻), bromide

(Br$^-$), thiocyanate (SCN$^-$), and azide (N$_3^-$) anions. Different class of ILs can produce, upon irradiation, different reactive intermediates. Therefore, they can provide a new environment induced by radiation in which to test radical reactions including charge transfer processes [1, 115-117].
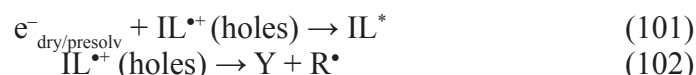
4.1. INITIAL EVENTS IN RADIOLYSIS

Ionization (Eq. (98)) and excitation (Eq. (99)) are the two major processes occurring in ILs:

$$IL \text{ -}^{\wedge\wedge\wedge\wedge\wedge}\rightarrow IL^{\bullet+} \text{(holes)} + e^- \text{(energetic electrons)} \tag{98}$$

$$IL \text{ -}^{\wedge\wedge\wedge\wedge\wedge}\rightarrow IL^* \tag{99}$$

The energetic electrons start to lose their excess kinetic energy and become "thermalized". Since they are not equilibrated with the surrounding molecules they are called either "dry" or "presolvated". As the solvation process proceeds, the electrons become more and more localized and eventually solvated (Eq. (100)):

$$e^- \rightarrow e^-_{dry/presolv} \rightarrow e^-_{solv} \tag{100}$$

"Holes" resulting from ionization (Eq. (98)) can undergo either recombination with electrons (Eq. (101)) or fragmentation of any type (Eq. (102)) [116, 117]:

$$e^-_{dry/presolv} + IL^{\bullet+} \text{(holes)} \rightarrow IL^* \tag{101}$$

$$IL^{\bullet+} \text{(holes)} \rightarrow Y + R^{\bullet} \tag{102}$$

4.2. SELECTED RADICAL REACTIONS INVOLVING HOLES AND ELECTRONS

In the presence of electron scavengers, both types of electrons can form radical anions (Eq. (103)):

$$e^-_{presolv/solv} + S \rightarrow S^{\bullet-} \tag{103}$$
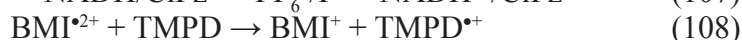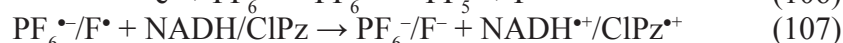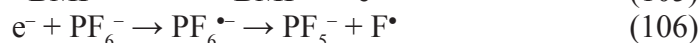
where S designates different types of electron scavengers: those reacting with either presolvated or solvated electrons and those reacting with both of them. In the presence of "hole" scavengers the respective solute radical cations can be formed (Eq. (104)):

$$IL^{\bullet+} \text{(holes)} + S \rightarrow S^{\bullet+} \tag{104}$$

Only a few examples of radiation-induced radical reactions in IL containing 1-butyl-3-methyl-imidazolium cation (BMI$^+$) will be presented.

The radical cations from 1-methyl-1,4-dihydronicotinamide (NADH), chlorpromazine (ClPz), and N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD) (Eqs. (105)-(108)), and both the radical cations and anions from benzoquinone (BQ), duroquinone (DQ), methyl viologen (MV), chlorpromazine (ClPz), 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) and

thiophene and its derivatives were generated in this IL containing hexafluorophosphate (PF_6^-) or tetrafluoroborate (BF_4^-) anions [118, 119].

$$BMI^+ \text{-}\wedge\wedge\wedge\wedge\wedge\rightarrow BMI^{\bullet 2+} + e^- \qquad (105)$$

$$e^- + PF_6^- \rightarrow PF_6^{\bullet -} \rightarrow PF_5^- + F^\bullet \qquad (106)$$

$$PF_6^{\bullet -}/F^\bullet + NADH/ClPz \rightarrow PF_6^-/F^- + NADH^{\bullet +}/ClPz^{\bullet +} \qquad (107)$$

$$BMI^{\bullet 2+} + TMPD \rightarrow BMI^+ + TMPD^{\bullet +} \qquad (108)$$
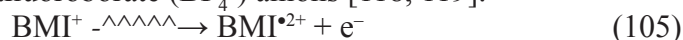
Dihalide ($Cl_2^{\bullet -}$ and $Br_2^{\bullet -}$) and pseudohalides (($SCN)_2^{\bullet -}$ and $N_6^{\bullet -}$) have been selectively generated in this IL with Cl^-, Br^-, SCN^-, and N_3^- anions (Eqs. (105), (109) and (110)) [120]:

$$BMI^{\bullet 2+} + Cl^-/Br^-/SCN^-/N_3^- \rightarrow BMI^+ + Cl^\bullet/Br^\bullet/{}^\bullet SCN/N_3^\bullet \qquad (109)$$

$$Cl^\bullet/Br^\bullet/{}^\bullet SCN/N_3^\bullet + Cl^-/Br^-/SCN^-/N_3^- \leftrightarrows Cl_2^{\bullet -}/Br_2^\bullet/(SCN)_2^{\bullet -}/N_6^{\bullet -} \qquad (110)$$
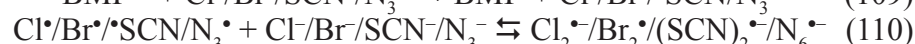
Providing a comprehensive review of radical reactions occurring in ILs in the absence and in the presence of various solutes is beyond the scope of this text.

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