RADICAL REACTIONS WITH METAL COMPLEXES IN AQUEOUS SOLUTIONS

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Summary

Due to their unpaired electrons radicals are highly reactive species. They play an important role in combustion, atmospheric chemistry, polymerization, plasma chemistry, biochemistry, and many other chemical processes, including human physiology. The role of radicals in living systems is dual. On the one hand radicals are vital for normal biological functions but on the other hand they are responsible for a variety of deleterious biological processes. Thus a guarded balance of radical species is imperative.

Transition metal complexes are key participants in biological and catalytic radical processes due to two major reasons:

- radicals are usually generated by redox reactions involving transition metal complexes
- the majority of secondary radicals formed in biological and/or catalytic systems react much faster with transition metal complexes than with organic substrates. Therefore the participation of the transition metal complexes determines the nature of the final products.

Important types of radicals, i.e. inorganic, organic and stable radicals, are described briefly and the participation of transition metal complexes in radical chemistry is reviewed.

1. Radicals and Their Role in Chemical Processes with Emphasis on Biological Systems

In chemistry radicals are defined as atomic or molecular species with unpaired electrons (transition metal complexes with unpaired electrons in d or f orbitals are not included in this definition). In molecular orbital theory, this state is represented by a singly occupied molecular orbital or SOMO. These unpaired electrons are usually highly reactive and consequently radicals are likely to take part in chemical reactions. Several exceptions exist, thus dioxygen is a stable biradical and nitric oxide (NO) as well as nitric dioxide are considered stable radicals. These types of radicals are relatively unreactive but react rapidly with molecules that have unpaired electrons in their outer orbital (typically other radicals or low valent transition metal complexes). Radicals thus play an important role in combustion, atmospheric chemistry, polymerization, plasma chemistry, biochemistry, and many other chemical processes, including human physiology.

Indirect evidence implies that radicals play a key role in both normal biological functions and in the pathogenesis of certain diseases.

Radicals are implicated in certain vital biological processes, e.g. several essential enzymatic processes such as photosynthesis and the biosynthesis of DNA (ribonucleotide reductases), in B_{12} catalyzed processes, cell-signaling (neuromodulators), xenobiotic metabolism (fate of foreign compounds in biological

systems), mediators in inflammatory processes or killing of bacteria by neutrophil granulocytes (antimicrobial defense).

Alternatively radical reactions may result in cell damage. It is commonly accepted that radical reactions play a major role in aging and in a variety of catalytic and biological processes. These processes include e.g. reactions involving ROS (Reactive Oxygen Species; including $^{\bullet}OH$, superoxide radicals, and peroxides, e.g. H_2O_2, alkyl peroxides, the latter act as a source of radicals) and RNS (Reactive Nitrogen Species, such as $NO^{\bullet}$ (nitric oxide) and its by-products $NO_2^{\bullet\cdot}$ (nitrogen dioxide), nitrate (NO_3^-), nitrite (NO_2^-), peroxynitrite ($ONOO^-$), and 3-nitrotyrosine)).

In biology 'Fenton like' reactions are believed to be the main source of ROS in the body causing a variety of diseases, e.g. cancer, atherosclerosis, essential hypertension, Alzheimer's disease, Parkinson's disease, amyloidosis, osteoarthritis, etc.. Superoxide radicals are further produced as a byproduct of the dioxygen reduction in the mitochondria. The role of nitric oxide (NO) in mammalian biology include cytotoxic immune response to pathogen invasion and cellular signaling in the cardiovascular and nervous systems. Metal centers are primary targets and reactions with dioxygen and other reactive oxygen species produce NO_x intermediates, which have important physiological roles. Nitric oxide has also been reported to inhibit metalloenzymes such as catalase and cytochrome oxidase, and its vasodilator properties have been implicated in blood pressure regulation by virtue of its action on the vascular smooth muscle. The interaction of NO with hemoglobin leads to the formation of S-nitrosothiols, SNO. SNO is formed when oxidized NO interacts with the highly reactive thiol groups on the two cystein residues in the hemoglobin molecule. Numerous disease states have been shown to involve the over- or under-production of NO.

In addition radicals contribute to alcohol induced liver damage and radicals in cigarette smoke (mainly alkoxyl radicals, NO and NO_2) promote the development of emphysema in the lungs due to inactivation of alpha 1-antitrypsin. Likewise an association between radical generating metals, such as iron or copper, and radical related clinical manifestations are explained by the involvement of these metals in the formation of radicals via 'Fenton like' reactions. e.g. Hemochromatosis, an excess of iron stores in the body, produces a number of radical related symptoms (arthritis, deafness, melanin abnormalities, psychosis, diabetes). Acute radical pathogenesis consequently occurs under conditions of exceptionally high radical flux. This includes radiation, inflammation, high oxygen tension and xenobiotic metabolism.

Due to the necessity of radical processes occurring in the body at specific levels of radical concentration opposed to the need to counter their unwanted side reactions, a number of mechanisms to minimize or repair radical induced damage are present in the cell. Enzymes, which act as inhibitors of radical formation, as radical scavengers or chain reaction terminators, are e.g. superoxide dismutase (SOD), catalase and gluthathione peroxidase and reductase. 'Solid state' defenses such as melanin exist, which is an antioxidant bio-polymer and forms one of the longest living radicals in itself. Furthermore a range of chemical antioxidants is liable to protect the cell by

donating electrons (being 1-electron reductants) to neutralize the radicals, e.g. the vitamins A, C and E and also bilirubin, uric acid and gluthathione. By neutralizing the radicals however the radicals of the respective antioxidant are formed; moreover the antioxidant concentration and other chemical conditions (such as pH, availability of metal catalyst, oxygen concentration, etc.) are extremely sensitive, as high or low doses or a shift in chemical conditions might induce a prooxidant effect of the same antioxidant. Thus in the body a careful equilibrium of processes has to occur in order to prevent or diminish radical induced deleterious processes.

2. The Chemistry of Radicals

2.1. Initiation, Propagation, Termination

These definitions are important to radical chemistry. Radical processes are usually separated into these three stages. Initiation reactions result in a net increase in the number of radicals. This may be due to the formation of radicals from stable species by e.g. bond homolysis, by redox reactions often with transition metal complexes or by the reaction of radicals with stable species to form more radicals (see also formation of radicals in the following section).

During the propagation reactions the total number of radicals remains the same. Due to their reactivity radicals generally react with solution constituents (molecules, atoms, other radicals) in long series of chain reactions, well established in the classic case of combustion or polymerization chemistry.

Termination reactions result in a net decrease in the number of radicals, typically by the combination of two radicals to form a stable species $(R^{\bullet} + R'^{\bullet})$ or by a redox process with a transition metal complex $(R^{\bullet} + ML)$. The reactions between two radicals are rather rare processes as radicals are normally present at low concentrations in a reaction medium, and it is statistically more likely that they will abstract a hydrogen, or undergo another type of a substitution process, rather than reacting with each other by coupling. Furthermore radicals are usually uncharged, so that there is little long-range coulombic attraction between two radical centers. Thus the propensity for chain reactivity in radical chemistry is rationalized.

2.2. Formation of Radicals

Radicals can be formed by several different mechanisms:
(a) Absorption of ionizing radiation in the medium, e.g. in dilute aqueous solutions initially forming:

$$H_2O \xrightarrow{\gamma, e^-} e^-aq\ (2.65),\ {}^{\bullet}OH\ (2.65),\ H^{\bullet}\ (0.60),\ H_2\ (0.45),\ H_2O_2\ (0.75),\ H_3O^+\ (2.65) \qquad (1)$$

where the values in parentheses are the number of molecules of a given product formed by the absorption of 100 eV in the medium. The radicals thus formed are powerful

redox reagents, *i.e.* e^-_{aq} ($E°$ = -2.87 V) is a strong reducing agent; $H^\bullet$ ($E°$ = ±2.31 V) is an equally strong reducing and oxidizing agent and $^\bullet OH$ ($E°$ = +2.73 V) is a powerful oxidizing agent. Thus a mixture of strong single electron oxidizing- and reducing-agents is formed.

The primary radicals formed can be transformed into a variety of secondary inorganic radicals determined by the solution composition

(e.g. $O_2^{\bullet-}$, $HO_2^\bullet$, $O_3^{\bullet-}$, $CO_2^{\bullet-}$, $CO_3^{\bullet-}$, $CN^\bullet$, $N_3^\bullet$, $^\bullet NH_2$, $^\bullet NO$, $^\bullet NO_2$, $^\bullet NO_3$, $NCO^\bullet$, $PO_3^{\bullet 2-}$, $PO_4^{\bullet 2-}$, $HS^\bullet$, $RSSR^\bullet$, $SO_2^{\bullet-}$, $SO_3^{\bullet-}$, $SO_4^{\bullet-}$, $SO_5^{\bullet-}$, $(SCN)_2^{\bullet-}$, $SeO_3^{\bullet-}$, $HSeO_4^{\bullet 2-}$, $(SeCN)_2^{\bullet-}$, $Cl_2^{\bullet-}$, $Br_2^{\bullet-}$, $I_2^{\bullet-}$, $ClO_2^\bullet$, $BrO_2^\bullet$, $IO_2^\bullet$)

and mainly via hydrogen abstraction from suitable organic solutes into organic radicals

(e.g. $^\bullet CH_3$, $^\bullet CH_2CH_3$, $^\bullet CH_2CH_2CH_3$, $^\bullet CH(CH_3)_2$, $^\bullet C(CH_3)_3$, c-$^\bullet C_5H_9$, $^\bullet CH_2Cl$, $^\bullet CH_2Br$, $^\bullet CF_3$, $^\bullet CCl_3$, $^\bullet CBr_3$, $^\bullet CH_2OH$, $^\bullet CH(CH_3)OH$, $^\bullet C(CH_3)_2OH$, $^\bullet CH_2CH_2OH$, $^\bullet CH_2C(CH_3)_2OH$, $^\bullet CH_2OCH_3$, $^\bullet CH(CH_3)OC_2H_5$, $^\bullet CH(OH)CH_2OH$, $^\bullet CH_2CHO$, $^\bullet CH_2CO_2H$, $^\bullet CH(CH_3)CO_2H$, $^\bullet CH(OH)CO_2H$, $^\bullet C(OH)(CH_3)CO_2H$, $^\bullet CH(CH_2NH_3^+)CO_2^-$, $^\bullet CH(CH_3)NH_2$, $^\bullet CH_2C(CH_3)_2NH_3^+$, $^\bullet CH_2CN$, $^\bullet CH_2C_6H_5$, $^\bullet SC_2H_5$, $CH_3OO^\bullet$, $CCl_3OO^\bullet$, $NCCH_2OO^\bullet$, $HO_2CCH_2OO^\bullet$, etc.)

Furthermore radicals can react with aromatics or unsaturated compounds by addition to double bonds.

b) Homolytic bond breakage of specific molecules induced by thermolysis or electromagnetic radiation or ultrasound cavitation.
c) Radical production by photochemistry. So-called photosensitizers absorb light (forming high yields of the triplet state). These excited molecules can further interact with solution components via e^- or H-atom transfer to produce organic radicals. Furthermore excited molecules can interact by energy transfer with dissolved oxygen to produce singlet oxygen, which is highly reactive.
d) Ultrasonic cavitation in aqueous solutions yields hydroxyl radicals and hydrogen atoms. The major products are $^\bullet OH$ radicals. The yield of radicals depends strongly on the nature of the gases in equilibrium with the solution and the temperature.
e) Alternatively, radicals can be generated by redox reactions involving transition metals (e.g. Fenton like reactions, vide infra). A variety of redox reactions of transition metal complexes with organic molecules producing radicals exist:

$$M^n + RX \rightarrow M^{n+1} + R^\bullet + X^- \qquad (2)$$

Reaction (2) basically represents the initiation step in 'Atom transfer radical polymerization' (ATRP), an example of living polymerization, which involves chain

initiation by a halogenated organic species in the presence of a metal halide species, creating a radical that then starts radical polymerization. After initiation and propagation, the radical on the active chain terminus is reversibly terminated by reacting with the catalyst in its higher oxidation state. Thus, the redox process brings about equilibrium between dormant (Polymer-Halide) and active (Polymer-radical) chains. The equilibrium is designed to heavily favor the dormant state, which effectively reduces the radical concentration to sufficiently low levels to limit bimolecular coupling and allow controlled polymerization.

Organohalides are severe environmental pollutants. Their toxicity is due to reaction (2), which produces radicals, which initiate deleterious biological processes. Also their dehalogenation via reaction (2) is important in pollution control.

$$M^{n+1} + RH \rightarrow M^{n} + R^{\bullet} + H^{+} \quad (3)$$

A classical example for reaction (3) is the catalytic oxidations of methyl-aryls by O_2, which is initiated by Co^{3+}.

$$PhCH_3 + Co^{3+} \rightarrow PhCH_2^{\bullet} + Co^{2+} + H^{+} \quad (4)$$

$$PhCH_2^{\bullet} + O_2 \rightarrow PhCH_2OO^{\bullet} \quad (5)$$

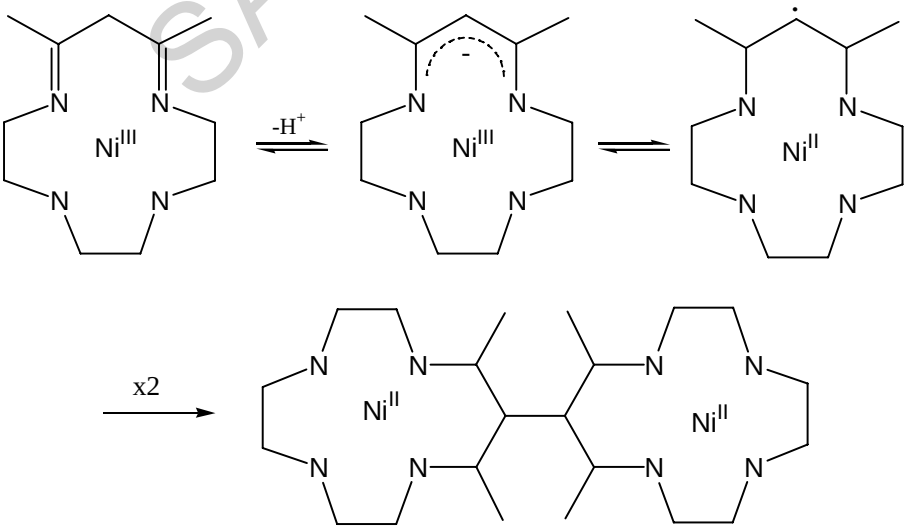
$$PhCH_2OO^{\bullet} + Co^{2+} \xrightarrow{H^{+}} PhCH_2OOH + Co^{3+} \quad (6)$$

$$PhCH_2OOH + Co^{2+} \rightarrow PhCH_2O^{\bullet} + Co^{III}(OH)^{2+} \quad (7)$$

$$PhCH_2O^{\bullet} + Co^{3+} \rightarrow PhCHO + Co^{2+} + H^{+} \quad (8)$$

Under appropriate conditions the aldehydes thus formed can be oxidized to the corresponding acids. The formation of $R^{\bullet}$ radicals by other high valent transition metal ions, e.g. Mn^{3+}, and Ce^{4+} is well documented.

Another example of reaction (3) is intramolecular redox reactions yielding radicals, e.g.:



(9)

A further mechanism, which yields $R^{\bullet}$ radicals is:

$$M^{n+1} + RCO_2^- \rightleftarrows M^{n+1}\text{-O-C(O)R} \rightarrow M^n + CO_2 + R^{\bullet} \quad (10)$$

i.e. a mechanism analogous to the Kolbe process.

Reaction (11) was studied in efforts to mimic the Cytochrome P-450 chemistry.

$$M^{n+2}\text{=O} + RH \rightarrow M^{n+1}\text{-OH} + R^{\bullet} \quad (11)$$

Though radicals are often implicated in these systems they are often very short lived as they react in the cage formed via:

$$M^{n+1}\text{-OH} + R^{\bullet} \rightarrow M^n + ROH \quad (12)$$

Production of radicals via transition metal complexes is also realized in a variety of enzymatic processes in biological systems, e.g. radicals are a byproduct of cellular respiration (stepwise transfer of electrons from NADH (and $FADH_2$) to oxygen molecules to form water molecules in a 4 electron reduction). Some electrons always leak in the early stages of the respiratory chain and reduce dioxygen molecules to the superoxide anion. $NO^{\bullet}$ is synthesized in cells by Nitric Oxide Synthases. Radicals like $NO^{\bullet}$ and $O_2^{\bullet -}$ are synthesized by dedicated enzymes in phagocytic cells like neutrophils and macrophages.

2.3. Redox Properties of Radicals

Many radicals are highly reactive, owing to the tendency of electrons to pair. Therefore, either the receipt of an additional electron from an appropriate donor pairs the electron in the singly occupied molecular orbital of the radical or that electron is donated to an appropriate acceptor. Thus the reactivity of radicals stems mainly from the fact that they are powerful one electron redox reagents. From a compilation of redox-potentials for a wide variety of radicals in aqueous solutions, Table 1 presents an overview of redox-potentials for some selected important inorganic and organic radicals.

Compound/couple	*E* /*V*
aq/e^-_{aq}	-2.87
$^{\bullet}H$	±2.31
$^{\bullet}OH/OH^-$	+1.9
$^{\bullet}OH, H^+/H_2O^{\bullet}$	+2.73
$O_2^{\bullet -}, H^+/HO_2^-$	+1.0
$O_2^{\bullet -}, 2H^+/H_2O_2$	+1.76

$HO_2^{\bullet}$, H^+/H_2O_2	+1.48
$HO_2^{\bullet}/HO_2^-$	+0.79
$O_2/O_2^{\bullet-}$	-0.33
NO/NO^-	~+0.8
NO^+/NO	+0.33
$NO_2^{\bullet}/NO_2^-$	+1.0
$CO_2^{\bullet-}$, H^+/HCO_2^-	+1.07
$CO_2/ CO_2^{\bullet-}$	-1.9
$Br_2^{\bullet-}/2Br^-$	+1.66
$Cl_2^{\bullet-}/2Cl^-$	+2.3
$I_2^{\bullet-}/2I^-$	+1.1
$N_3^{\bullet}/N_3^-$	+1.33
$(SCN)_2^{\bullet-}/2SCN^-$	+1.33
$SO_2^{\bullet-}$, H^+, H_2O/HSO_3^-	-0.66
$SO_3^{\bullet-}/SO_3^{2-}$	+0.72
$SO_5^{\bullet-}/HSO_5^-$	(+1.1) - (+1.7)
$CH_2O/^{\bullet}CH_2O^-$	-1.81
CH_2O, $H^+/^{\bullet}CH_2OH$	-1.18
$RS^{\bullet}$, H^+/RSH	+1.3
$HS^{\bullet}/HS^-$	+1.15
$CH_3O_2^{\bullet}/CH_3O_2H$	(+0.6)-(+0.7)

Table 1: Redoxpotentials of selected radicals in aqueous solutions

In theory electron transfer reactions may proceed via two distinct possible mechanisms:

- The outer sphere mechanism, where the electron is transferred between the redox couples, while the inner coordination shells of the respective reactants remain intact. No chemical bond between the reactants is formed.
- The inner sphere mechanism. A chemical bond is formed between the reactants prior to the electron transfer.

While it is commonly perceived that most electron transfer processes in biological systems proceed via outer sphere electron transfer mechanisms, these kinds of reactions are in fact rare for radicals. It has to be noted here, that most electron transfer processes of radicals do not transpire via simple outer sphere electron transfer processes. Generally electron transfer processes proceed in an outer sphere mechanism, only when the reaction does not require major bond rearrangements and therefore the self exchange rates of the couples are high. Even most of the simple radicals described in table 1 do not adhere to the requirements for outer sphere electron transfer. Most uncharged

radicals will be converted into charged entities due to the electron transfer and thus intrinsically have distinctly higher solvation energy than the originally uncharged species. Thus for example $H^{\bullet}$ or $^{\bullet}OH$ radicals basically only have small hydration energies, while their one electron redox products H^{+} or OH^{-} respectively possess high solvation energies. The reduced product of $H^{\bullet}$, H^{-} on the other hand is unstable and requires the follow up reaction with H^{+} to form H_2 for the reaction to proceed. $CO_2^{\bullet-}$ for example is a powerful reducing agent but as it is bent and its oxidized product CO_2 is linear most of its reactions proceed via the inner-sphere mechanism. For the reactions of $X_2^{\bullet-}$ to form X_2^{2-} the latter are unstable and therefore the reactions do not proceed via outer sphere mechanisms. $N_3^{\bullet}$ on the other hand is a strong outer sphere oxidizing agent, as N_3^{-} does not have high hydration energy.

All the organic radicals are relatively strong single electron oxidizing and reducing agents. The redox properties of aliphatic carbon-centered radicals depend on the substituents on the α-carbon.

Thus for example radicals of the type $^{\bullet}CR^1R^2(OH)$ are relatively strong reducing agents; however they do oxidize low-valent transition metal complexes, e.g. $Cr(H_2O)_6^{2+}$ and $V(H_2O)_6^{2+}$. On the other hand $^{\bullet}CCl_3$ and $^{\bullet}CH_2CO_2H$ and alkyl-peroxyl radicals are relatively strong oxidizing agents. As the self exchange rates for the $R^{\bullet/-}$ and $R^{+/\bullet}$ couples are usually slow, and as the products R^{+} and R^{-} are highly unstable, outer sphere reactions are not abundant for these types of molecules. However outer-sphere reductions of transition metal complexes by $^{\bullet}CR^1R^2OH$ or $^{\bullet}CR^1R^2O^{-}$ radicals were observed. This is reasonable as these radicals are powerful reducing agents and as the oxidation of these radicals does not require major bond rearrangements. Thus the self exchange rate for the couple $C(CH_3)_2OH^{+/0}$ has been estimated to be ~10^3 $M^{-1}s^{-1}$.

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Biographical Sketches

Dan Meyerstein was born in Jerusalem, Israel, in 1938. He received his M.Sc., in 1961, and Ph.D., in 1965, at The Hebrew University of Jerusalem. After a postdoctoral fellowship at Argonne National Laboratory in IL, he joined the faculty of the Ben-Gurion University, where he is presently a Professor Emeritus. Since 1995, he has been President of The College of Judea and Samaria in Ariel, Israel. He was president of the Israel Chemical Society. He received the Humboldt-Meitner research prize and the Kolthof prize. His research interests include mainly the kinetic and mechanistic studies of redox processes of transition-metal complexes in aqueous solutions with an emphasis on radical processes.

Alexandra Masarwa was born in Bonn, Germany, in 1958. She received her B.Sc., M.Sc., and Ph.D. in chemistry from the University of Cologne in Germany. She attained her Ph.D. in inorganic chemistry in 1987 under the supervision of Prof. Fritz Wasgestian. She spent two sabbatical years (1987-1989) under the supervision of Prof. Dan Meyerstein in Beer Sheva, Israel studying metal carbon σ bond chemistry and an additional 4 years (1989-2003) with Prof. Daryle H. Busch in Lawrence, Kansas, USA studying oxygen carrier analogues. Since 1994, she has been employed by the Ben Gurion University as a senior research scientist in the Chemistry Department.