## Can Innovative Chemical Technologies Improve Radical Chemistry?

## **Estelle Banaszak Leonard**

ESCOM, France

## **Abstract:**

Radical chemistry is of great interest in many chemical areas, like medicinal chemistry, material chemistry or polymers, or maybe formulation, so as to know and stop radical disorders. However, despite the lasting interest in performing radical syntheses, the use of innovative techniques for a more eco-friendly approach remains occasional. We will focus on examples showing how natural products can undergo radical transformations under innovative techniques. It will be shown that the combination of uncommon energetic devices with greener solvent can shorten reaction times, or even promote the envisioned reaction. By using aromatic aldehydes, (un)modified aminoacids or fatty acids, the molecules from such radical processes can be used in a wide range of applications. Biocides, surfactants, electron-transfer materials or even synthons are real options for molecules valorization.

## **Introduction:**

Radical, also called radical, in chemistry, molecule that contains a minimum of one unpaired electron. Most molecules contain even numbers of electrons, and therefore the covalent chemical bonds holding the atoms together within a molecule normally contains pairs of electrons jointly shared by the atoms linked by the bond. Most radicals may be considered to have arisen by cleavage of normal electron-pair bonds, every cleavage having produced two separate entities, each of which contains a single, unpaired electron from the broken bond (in addition to all the rest of the normal, paired electrons of the atoms).

Although free radicals contain unpaired electrons, they'll be electrically neutral. Because of their odd electrons, free radicals are usually highly reactive. They combine with one another, or with single atoms that also carry free electrons, to give ordinary molecules, all of whose electrons are paired; or they react with intact molecules, abstracting parts of the molecules to finish their own electron pairs and generating new free radicals within the process. In all these reactions, each simple radical, due to its single unpaired electron, is in a position to mix with one other radical or atom containing one unpaired electron. Under special circumstances, diradicals can be formed with unpaired electrons, and these diradicals have a combining power of two.

Certain free radicals are stabilized by their peculiar structures; they exist for appreciable lengths of time, given the right conditions. Most free radicals, however, including such simple ones because the methyl (•CH3) and ethyl (•C2H5) radicals, are capable of only the foremost fleeting independent existence. The first relatively stable radical, triphenylmethyl (structure I), was discovered by Moses

Gomberg in 1900. In this compound the central carbonis trivalent since it is combined with three substituents instead of four, and its unshared electron is represented by a dot. Free radicals of the triphenylmethyl type are stable only in certain organic solvents; they are rapidly destroyed by irreversible reactions in the presence of air, water, or strong acids.

In a manner analogous to the above, free radicals are formed by the breaking of the nitrogen–nitrogen bond in aromatic hydrazines of the general structure R2N-NR2, or of the central nitrogen–nitrogen bond in aromatic tetrazanes, R2N-RN-NR-NR2. Thus, the radical 1,1-diphenyl-2-picrylhydrazyl (structure II) exists as a stable violet solid. Similar samples of free radicals, in which, however, the odd electron is on oxygen, tri-tert-butylphenoxy radical (structure III).



Image 1: Chemical Structures.

Still another sort of stable radical ion, a metal ketyl, forms when a substance like benzophenone, is treated with metallic sodium to offer the coloured substance (C6H5)2C-O. Similarly, sodium reacts with complex aromatic hydrocarbons like naphthalene, converting them to highly coloured radical ions.

A final class of relatively stable organic free radicals are those containing the group > NO. An example is diphenylnitrogen oxide, (C6H5)2NO, which is obtained by the oxidation of diphenylhydroxylamine, (C6H5)2NOH. Certain structural features appear to be required for the existence of stable free radicals. One condition of particular importance is shown by the semiquinone radical ion IV. As depicted, the upper oxygen atom has a negative charge and the lower one an odd electron. This assignment is arbitrary,



Image 2.

however, and the same molecule would be represented if the charge and the odd electron were interchanged. When such a situation is encountered, the actual average distribution of electrons within the molecule is presumed not to be that of either of the structures just described but to be intermediate between the two. This circumstance is called delocalization, or resonance; according to quantum mechanics, the resonance considerably increases the stability of the substance and, as in this case, the probability of its existence. Similar arguments account for the steadiness of the opposite free radicals discussed earlier.

Simple free radicals like methyl, •CH3, also exist and play key roles as transient intermediates in many chemical reactions. The existence of the methyl was first demonstrated by Friedrich A. Paneth and W. Hofeditz in 1929 by the following experiment. The vapours of tetramethyllead, Pb(CH3)4, mixed with gaseous hydrogen, H2, were skilled a silica tube at low . When some of the tube was heated to about 800° C, the tetramethyllead was decomposed and a mirror of metallic lead deposited on the interior surface of the tube. The gaseous products of the decomposition were found capable of causing the disappearance of a second lead mirror, deposited at a more distant cool point in the tube. Since none of the recognized stable products of the decomposition was able

similarly to dissolve a lead mirror, the inference was drawn that methyl radicals formed in the high-temperature decomposition reacted with lead at the cool mirror to regenerate tetramethyllead. Methyl radicals obtained during this way proved to be highly reactive and short-lived. They not only reacted with lead and other metals but also disappeared rapidly and spontaneously, largely by dimerization to ethane, H3C-CH3. Techniques for producing reactive free radicals in the gas phase have been greatly extended by subsequent research. It has been found that various unstable species, such as ethyl, (•C2H5), propyl, (•C3H7), and hydroxyl, (•OH), can be obtained by several methods including: (1) photochemical decomposition of a variety of organic and inorganic materials, (2) reaction between sodium vapour and an alkyl halide, and (3) discharge of electricity through a gas at low pressure. Atoms that arise from dissociation of a diatomic molecule (e.g., the chlorine atom, •Cl, from the dissociation of the chlorine molecule, Cl2) can also be obtained and have the properties of short-lived radicals of this type.