

THE OXIDATION STATES IN ORGANIC COMPOUNDS

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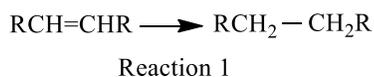
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ABSTRACT

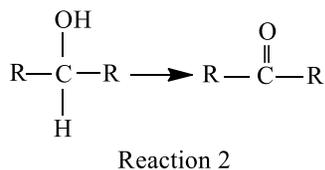
Presented is a method of assessment of the oxidation states of atoms in organic compounds. The method is a simple extension of the Pauling's electronegativity concept and is applied in various types of reactions including the biochemical processes of vital importance like neutralization of free radicals, β -oxidation or functioning of the nucleotide reductases. [*African Journal of Chemical Education—AJCE 11(2), July 2021*]

INTRODUCTION

Oxidation and reduction are two of the most frequent processes that occur in chemistry. Both of them were initially elucidated in the field of inorganic chemistry, which developed before organic chemistry. Oxidation means the loss (decrease) of electrons, and reduction of the gain (increase) of electrons. A concept of the oxidation state (OS) also referred to as the oxidation number in organometallic chemistry, [1] transmits the sense of the number of lost or gained electrons (totally or partially) by a predetermined atom during a reaction and reflects the capacity of this atom to lose or attract the shared electrons according to its electronegativity. Obviously, the more electronegative atoms show a greater tendency to attract electrons from neighboring atoms than the less electronegative atoms. This apparently well-established topic is still being debated. [1-3] Since the number of organic compounds far exceeds the number of inorganic compounds and the concepts of oxidation/reduction are widely used to describe the changes in the distribution of electrons during organic reactions, the question arises of how to evaluate the oxidation states of atoms in organic compounds. For example, the processes shown below are presented in didactic texts as reduction (Reaction 1) and oxidation (Reaction 2)



without explanation or comment



on changes in oxidation states in substrates and products.

In general, in organic chemistry, the criteria of increase or decrease of hydrogen and oxygen atoms in the molecule are used to identify reduction and oxidation. These criteria are not universal, because there are reactions where the number of oxygen atoms attached to a carbon atom in the molecule is increased (reaction 3), and the oxidation



Reaction 3

state of this carbon is not changed (see below).

Of the current books on organic chemistry for undergraduate courses that were consulted [4-9], none presents a chapter on the determination of oxidation states in organic compounds, including one of the most comprehensive book in the area. [7] Carey's book [10] has a short paragraph on oxidation states, but the treatment is very superficial. A strange situation is thus created: the concepts of oxidation/reduction in organic chemistry are used without a clear didactic explanation of how to effectively calculate oxidation states, that is, how to perform the evaluation of changes in these numbers and decide where the losses (oxidation) or gains (reduction) of electrons occur, which translate into the increase and decrease of oxidation states. This situation becomes even more bizarre considering the articles in the Journal of Chemical Education dedicated to the topic of oxidation states/numbers. [11-28] It can even be concluded that the authors of the textbooks have a certain fear of discussing this topic, probably to avoid criticism considering some consequences of OSs assessment, one of them being the formation of "ionic atoms" [21] (see below) or some "unchemical" conclusions. [27,28] Advanced organic chemistry book [29] treats about the OSs but one cannot expect that undergraduate students would consult such material. So, the objective of this article is to show how to calculate oxidation states (OSs) in organic compounds, from the structural formulas. This method is the simple application of electron

redistribution rules as a consequence of electronegativity differences between the atoms involved, according to Pauling's original ideas. [30]

Oxidation States and Charges/Formal Charges

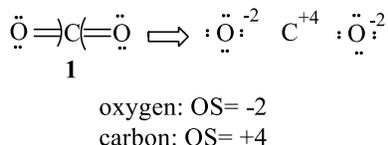
In organic chemistry, the basic concept of oxidation-reduction is the same as in inorganic chemistry: any bond between the atoms is treated as if it were ionic, according to the electronegativities of the atoms that compose it:

“The oxidation number of an atom in a molecule is the charge that this atom would acquire if the electrons of its covalent bonds to other atoms were attributed to the more electronegative atoms. In bonds between equal atoms the electrons are divided equally by the two atoms.” [28, 30]

Following this reasoning the most electronegative atom “moves” the electrons completely in its direction, regardless of the value of the difference between their electronegativities, [30] forming "ionic atoms".[28] It is already clear by now that the concept of oxidation number is **artificial**, but it is still very useful. This treatment is merely formal, **because the bonds in organic compounds are not ionic, they are overwhelmingly covalent bonds, where some are polarized.**

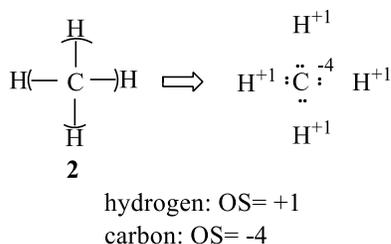
Let us see the electronegativities of the following atoms (Pauling scale) [27-29]: **B** 2.04; **Br** 2.96; **C** 2.55; **Cl** 3.16; **Cu** 1.90; **F** 3.98; **H** 2.20; **I** 2.66; **Li** 0.98; **Mg** 1.31; **N** 3.04; **O** 3.44; **P** 2.19; **S** 2.58; **Si** 1.90; **Sn** 1.91.

As a first example, let's evaluate the CO₂ molecule **1**:



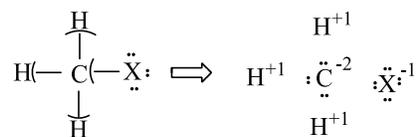
Considering the electronegativities of the carbon and oxygen atoms in **1**, it can be seen that the carbon atom "lost" all its four electrons from the outer layer, that is, it shows the absence of four electrons, and has the oxidation number +4. **We use the term "lost" to reinforce the idea that this is only about the counting of electrons and that it does not transmit the idea of ionic character of CO₂.** At the same time, the two oxygen atoms show the octets in the outer layer with two extra electrons, and the oxidation number -2 must be assigned to each one. One must realize that the sum of all the oxidation numbers in the neutral molecule is zero. **The treatment presented here is mere formalism, because CO₂ is not an ionic compound and the "ionic atoms" formed are the consequence of the electron count applied. The same comment is valid for all examples shown below. For the same reason, oxidation states cannot be used to discuss mechanistic considerations or reactivities of organic compounds (see below).**

Another example is the methane molecule **2**. Here, the carbon atom is linked to less



electronegative atoms and, therefore, following the same analysis criteria, the distribution of electrons is reached, as shown above. In this case, the carbon atom has four more electrons in its external layer, and an OS of -4 is attributed to it. Each one of the hydrogen atoms "lost" its electron and has an OS of +1. Since the molecule is neutral, the sum of all the OSs is zero.

The oxidation states of carbon atoms in organic compounds range between +4 and -4. In methyl halide **3**, any halogen atom (more electronegative than carbon) shows an OS of -1, regardless of the value of its electronegativity, carbon (less electronegative than



X = F, Cl, Br, I

3

X: OS = -1

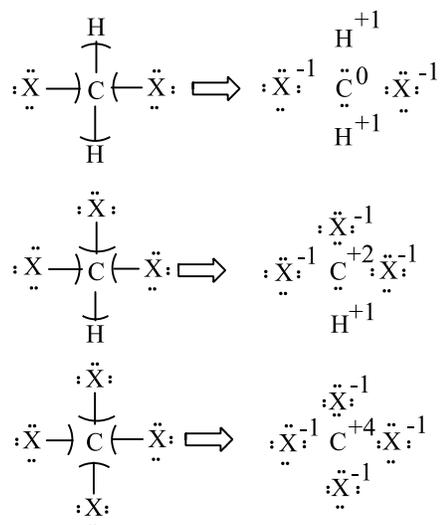
carbon: OS = -2

hydrogen: OS = +1

halogens) shows an OS of -2, and hydrogen (less electronegative than carbon) shows an OS of +1.

In most cases, the hydrogen atoms that "lose" their electron show an OS of +1, with exceptions such as borane **30** (BH₃) or metal hydrides, where the OS of hydrogen is -1 (see below).

In the case of di-, tri- or tetrahalomethanes **4** the OSs of the halide atoms remain the same (-1), as do the OSs of the hydrogen atoms (+1), but there are changes in the OSs of the carbon atoms.



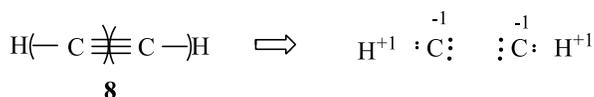
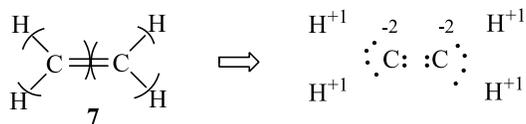
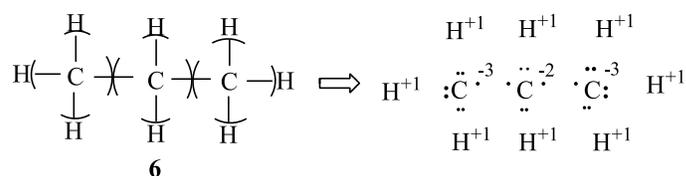
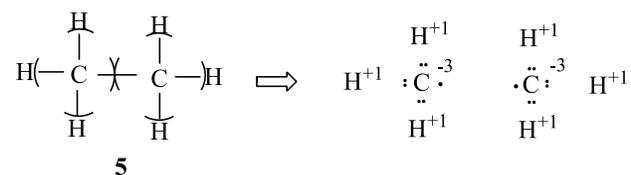
4: di-, tri- e tetrahalomethanes

X = F, Cl, Br, I

The increase of OSs of carbon atoms can be seen in the path of methane (OS -4), via methyl halides (OS -2), dihalomethanes (OS 0), trihalomethanes (OS +2) arriving at tetrahalomethanes (OS +4).

The ethane molecule **5** has a bond between two carbon atoms. In this case, the two electrons that form a symmetrical bond between the same atoms are divided.

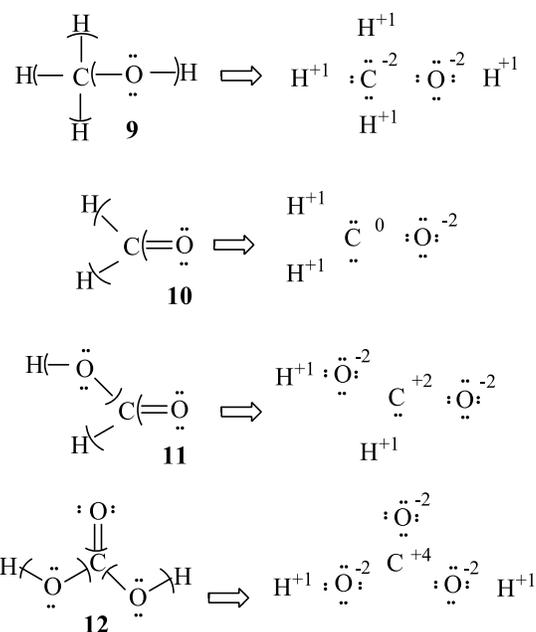
The same should be done to evaluate the OSs of propane **6**, ethylene **7** and acetylene **8**,



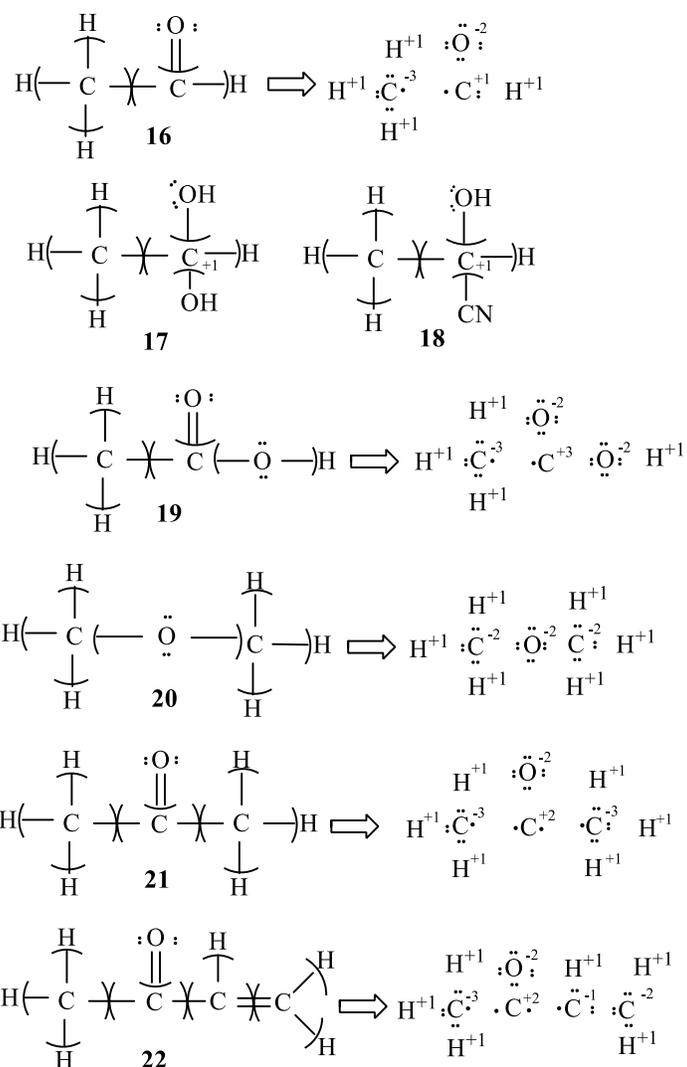
or any other saturated or unsaturated hydrocarbon. In general, bonds between the same atoms do not induce changes in the oxidation numbers of the atoms forming them. As mentioned above, hydrogen atoms show OSs +1 because they are bound to more electronegative atoms, and the OSs of carbon atoms depend on their position in the molecule. As a point of interest, one should mention that alternative method of ascribing the OSs to the carbon atoms in hydrocarbons based on the X-ray photoelectron spectroscopy has been suggested. [28]

When other compounds such as methanol **9**, methanal **10**, methanoic acid **11** and carbonic acid **12** are considered, it can be seen that the OSs of carbon atoms increase

and therefore methanol is said to be the product of methane oxidation, methanal is the oxidation product of methanol, and methanoic acid is the result of methane, methanol or methanal oxidation. CO₂ (and its unstable hydrated form **12**) is the most oxidized carbon compound, with OS +4, the same value as in tetrahalomethanes. The same increase in OS occurs when methane is progressively halogenated (compare OSs in **2**, **3** and **4**) and therefore the halogenation of methane (or any other hydrocarbon) is an oxidative process. One should notice that the OSs in the neutral and ionized compounds do not change, cf. **9** and **13a**, **11** and **14a** or **12** and **15a**.

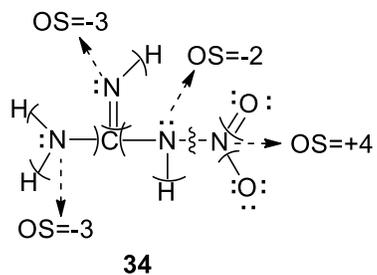
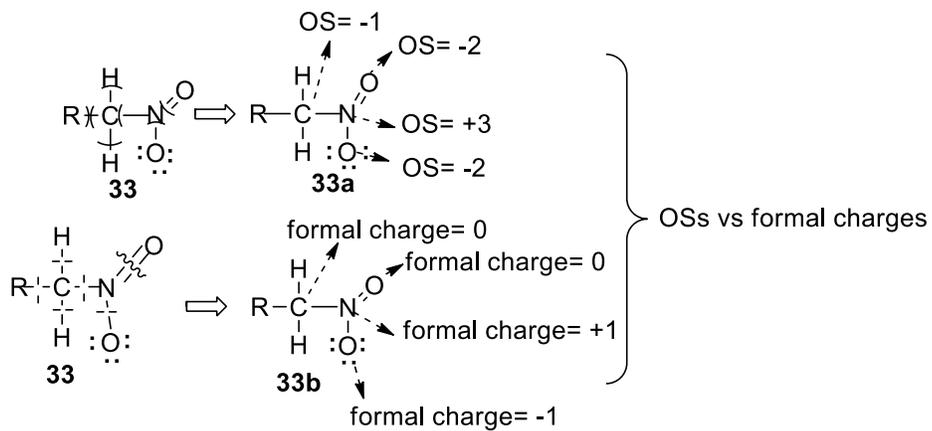
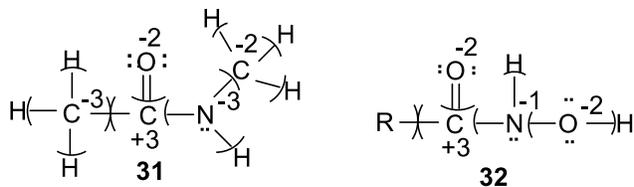
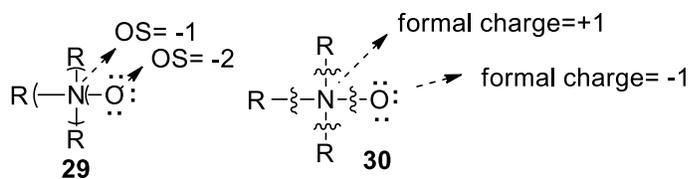
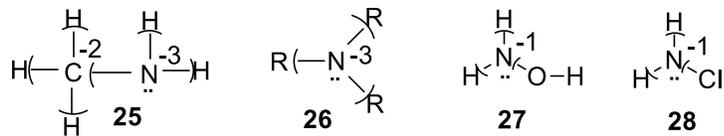


that, when the nitrogen atom is bound to carbon or hydrogen atoms (compounds **25**, **28**, **31**), its OS is -3; in cases of bonds with oxygen or chlorine as in **27**, **28**, **29** and **32**

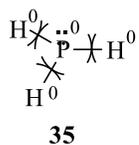


the OS is -1. In the case of the nitro compounds **33** the OS of the nitrogen atom is +3 because of the "loss" of electrons to oxygen, the more electronegative element. N-Nitroguanidine **34** is a compound where the nitrogen atoms display three different oxidation numbers. The difference between the OSs and the formal charges in the nitro group is shown in **33a** and **33b**, respectively.

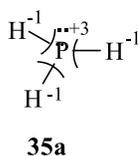
In some cases, as in PH_3 **35** (and other compounds where a P-H bond is found), or CS_2 **36** (or in general, where there is a C-S or C=S bond, as for example in thiocarbonate **37**),



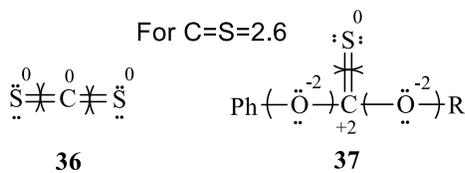
For P=H=2.2



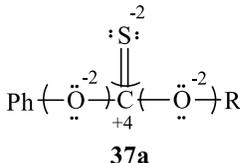
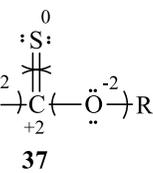
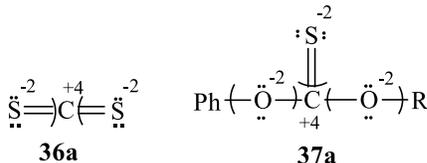
For P=2.19 and H=2.20



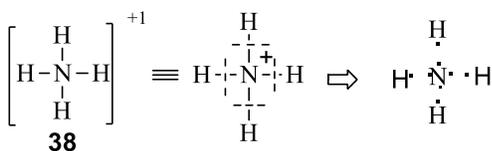
For C=S=2.6



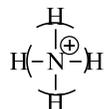
For C=2.55 and S=2.58



Evaluation of OSs using different electronegativities



Evaluation of formal charge: 4 electrons on N; formal charge+ +1

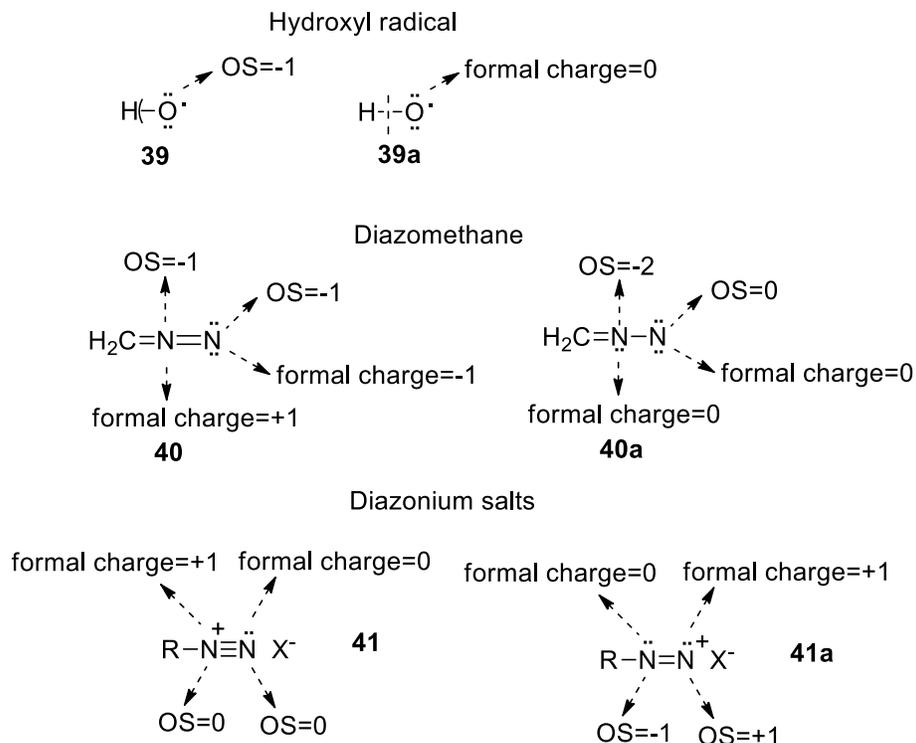


Evaluation of OS: 8 electrons on N; OS = -3

OS of H = +1 each

Balance: 4(+1) -3 = +1 \Rightarrow total charge of the cation

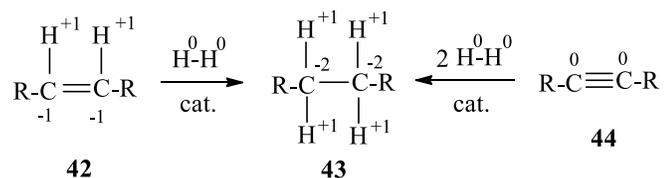
It is very useful to know how to identify the formal charges (or simply charges) in the atoms (lack or excess of electrons) and not to confuse them with the assignment of the oxidation states of these atoms (redistribution of electrons according to the electronegativities). The OSs vs. formal charges of **13**, **14**, **15** and **33** have already been discussed previously. To reinforce the different way of electron count to evaluate either the OSs or the formal charges, three additional examples (hydroxyl radical **39**, both resonance structures of diazomethane **40/40a** and diazonium salt **41/41a**) are shown.



Oxidation-reduction reactions: variation in oxidation states during organic reactions

Another objective of this article is to show the application of the rules of evaluation of oxidation numbers for some organic reactions, to show if the process is an oxidation or reduction reaction. This topic has already been briefly raised in the analysis of OSs for methane, methanol, methanal, methanoic acid and carbon dioxide.

As a first example, see the hydrogenation of alkenes **42** and alkynes **44**. Considering the

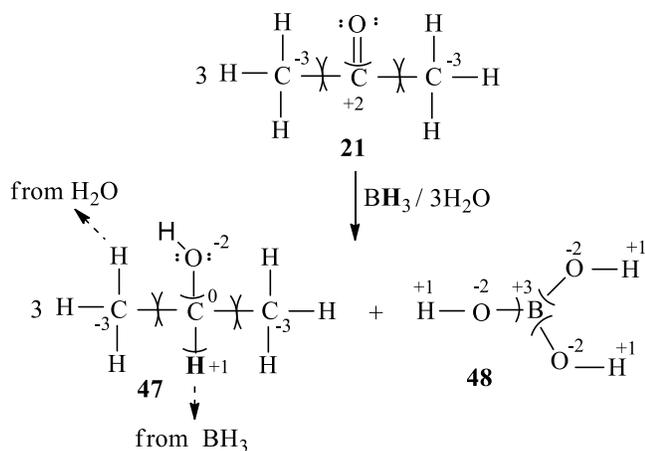
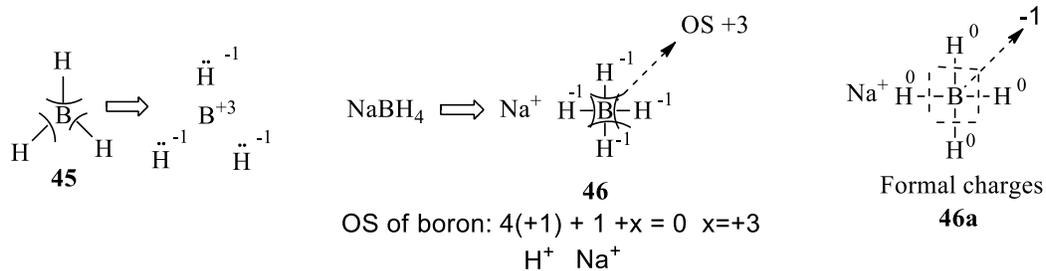


OSs in substrate **42** and in product **43**, it can be seen that there was a decrease in the OSs in the two carbon atoms during the addition of hydrogen, that is, that there was a reduction (change

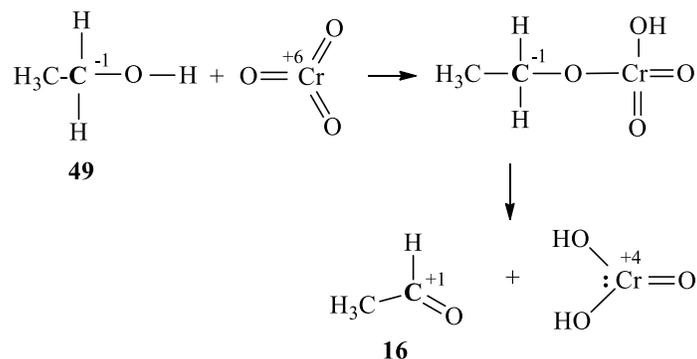
of OS from -1 to -2). The same type of reaction occurred during the hydrogenation of alkyne **44** (change of OS in carbon from 0 to -2). For this reason, the process in question is alternatively called a catalytic reduction. It is necessary to realize that the term "reduction" refers to the OS changes of the carbon atoms. However, from the point of view of the hydrogen atoms that were added to the multiple bonds, the process should be called oxidation, because they experienced "losses" of their electrons (change from OS=0 in the H₂ molecule, to OS= +1 in the products).

Another example is the reduction of acetone **21** using borane **45**, as shown below.

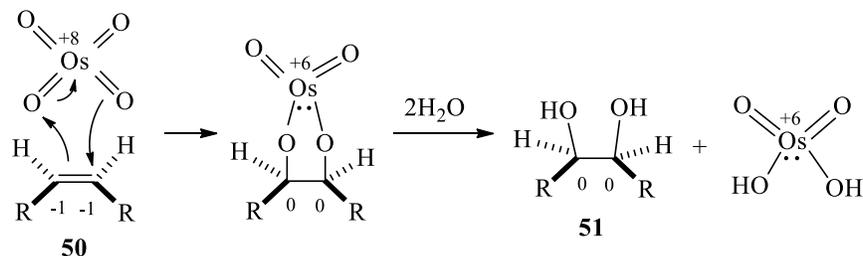
The molecule of borane **45** (or rather its dimer B₂H₆) is one of the rare examples where hydrogen atoms show OS -1, because boron is less electronegative than hydrogen. The borane serves as a donor to three H⁻ anions which bind to the carbon atoms of the carbonyl groups. The changes in the OSs of these carbon atoms (from +2 to 0) show that reduction has occurred. The use of borane (gas) is very inconvenient. In practice, its solid equivalent, NaBH₄ **46**, is used. In this, each hydrogen has two electrons around it (OS -1) and the boron has no electron (OS +3), whereas its charge is -1 as shown in **46a**. This undoubtedly confusing situation is a consequence of different ways of electron counting. Additionally, looking at the boron atom in **46** one could conclude that it "lost" four electrons. It is not possible since the boron atom has only three electrons available on the external shell. To visualize better the OS of boron in **46**, a balance similar to this of **38** should be done.



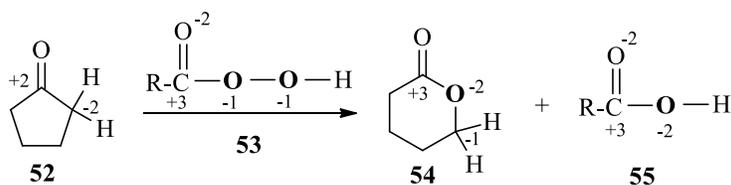
Regarding the oxidation of an alcohol using, for example, CrO_3 , it can be noticed that the carbon atom increased its OS from -1, in substrate **49**, to +1, in product **16**, that is, there was oxidation of this carbon atom, accompanied by the reduction of the chromium atom, which acted as an oxidant. Note that OS of the chromium is determined in the same way as for the carbon atoms.



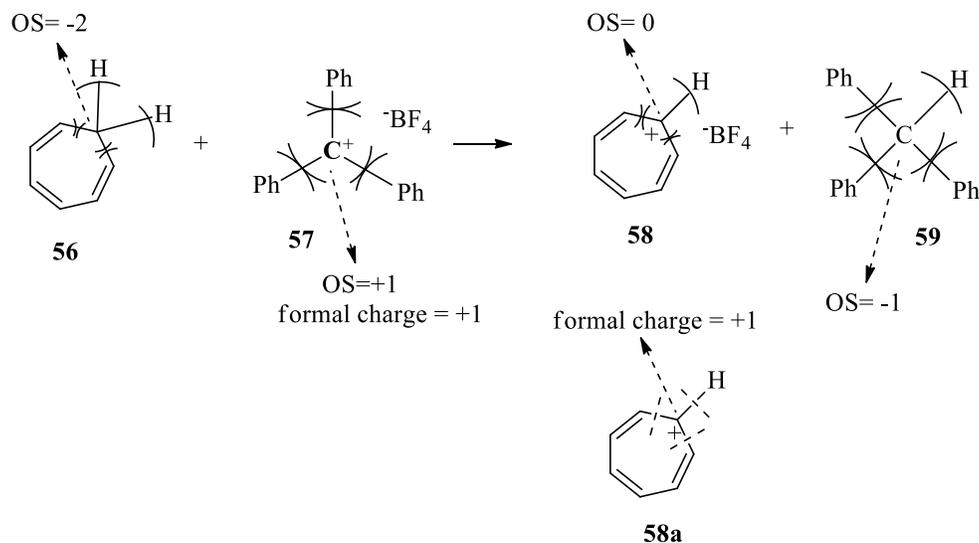
Another example is the *cis*-hydroxylation of alkene **50** using OsO_4 . This process is an oxidation, considering the increase in OSs of the two carbon atoms.



The Baeyer-Villiger process is another oxidation reaction. As in the case of *cis*-hydroxylation, the two marked carbon atoms in ketone **52** increased their OS, that is, they were oxidized to form lactone **54**. The two highlighted oxygen atoms in peroxyacid **53** showing OS -1 have been reduced, as their OS has decreased to -2.

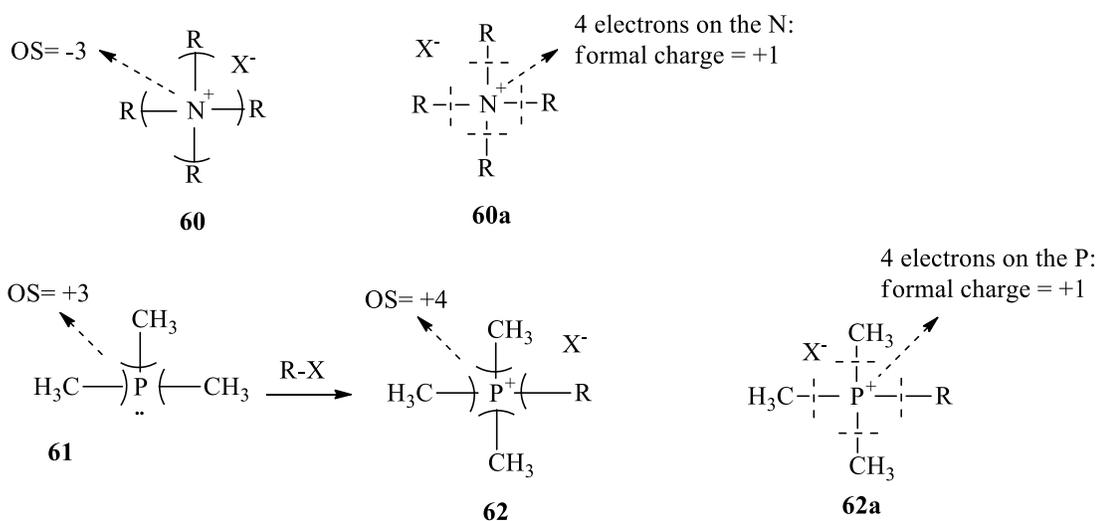


The changes in OS during oxidation using a carbenium ion such as Ph_3C^+ present in **57** [33, 34] are confusing, because the two concepts have to be used: oxidation number and the charge. For example, the cation Ph_3C^+ can receive an H^- anion from hydrocarbons, such as cycloheptatriene **56**, and form Ph_3CH **59** and a tropylium cation **58/58a**.



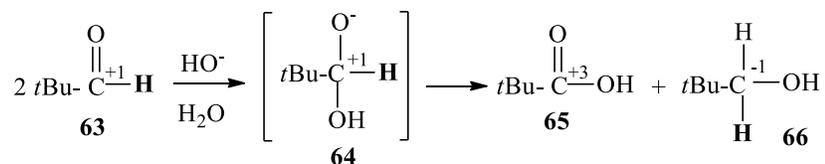
The highlighted carbon atom in **57** went from OS +1 to -1 in **59**; it was reduced and acted as an oxidant. In this example one can see application of the concepts of oxidation number (redistribution of electrons according to electronegativities) and of the formal charge (lack or excess of valence electrons) in the same carbon atom.

The same problem (OS vs. formal charge) exists for the ammonium salts **60/60a** or phosphonium salts **62/62a**. Similar examples have already been presented (**13/13a**, **14/14a**, **15/15a** and **38**).

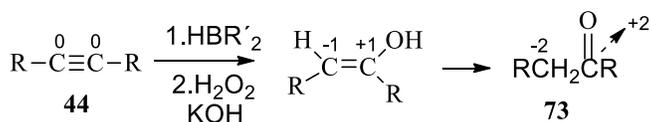
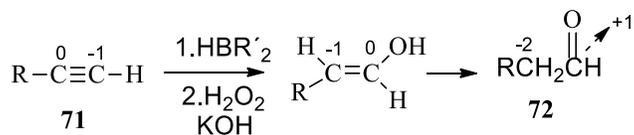
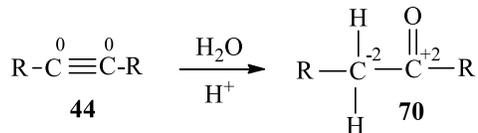
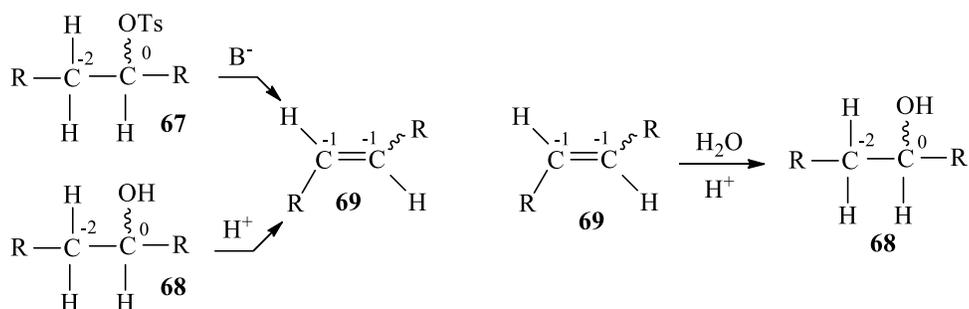


Another manifestation of changes in the OSs is the Cannizzaro reaction, a dismutation (or disproportionation) reaction, where a molecule of aldehyde without hydrogen in the α position, for example **63** is oxidized (\rightarrow **65**) and another is reduced (\rightarrow **66**) in an alkaline medium. The process is intermolecular, being the hydride anion (H^-) which transfers the two electrons between the two molecules via the intermediate **64**. It is not the objective here to discuss the mechanism of this process, but rather to observe the changes in OS in an example of a dismutation reaction.

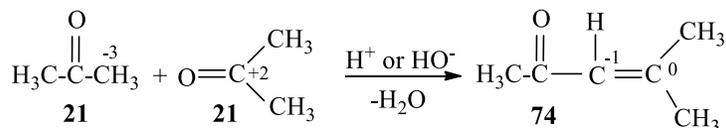
The other reactions in which different carbon atoms vary in their oxidation numbers, such as when obtaining alkenes **69** from tosylate (or mesylate, triflate, etc.) **67**



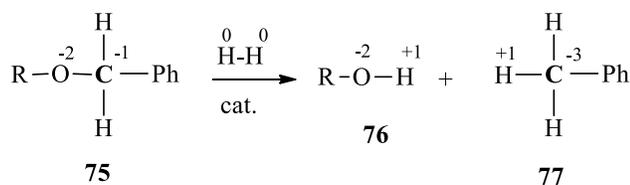
or from alcohols **68**, or when adding water to double (**69**→**68**) or triple (**44**→**70**) bonds, or during aldol condensation using acetone (**21**→**74**), are shown below.



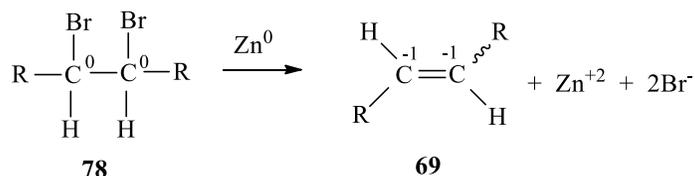
HBR'₂: disiamyl or dithexylborane



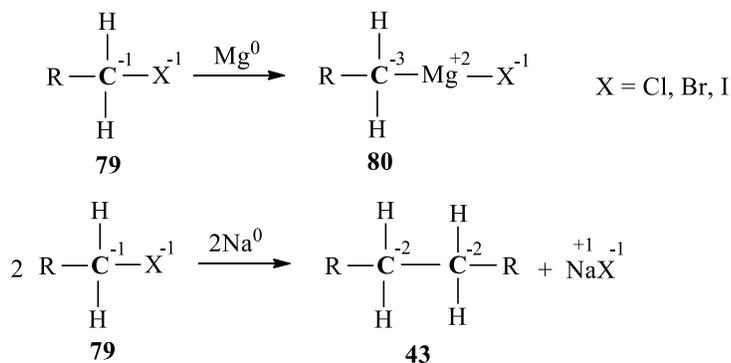
The alkoxy phenylmethyl ether breaking process is shown below. It can be seen that this reaction is a reduction by comparing the carbon atom OSs in **75** and **77**.



Alkenes can be obtained from vicinal bromides using zinc, which is one of the standard reactions taught in the organic chemistry. Considering the OSs of the carbon atoms in substrate **78** and in product **69**, it can be seen that reduction of the C atoms accompanied by oxidation of zinc has occurred. The number of hydrogen atoms in the substrate and in the product remains the same, but the OSs of

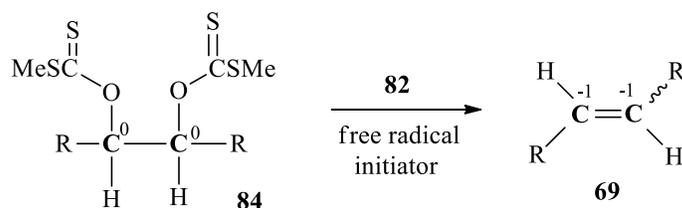
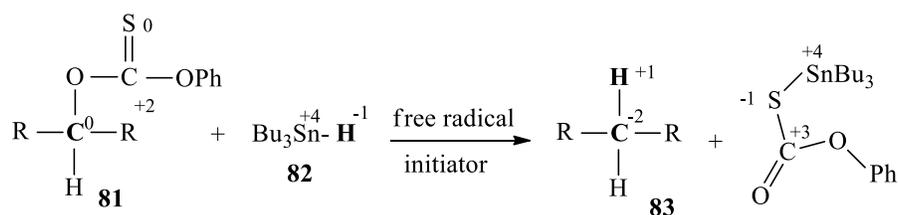


the two carbon atoms has decreased, i.e. reduction has occurred. For the reaction in the opposite direction, the addition of Br₂ to the C=C bond, oxidation occurred. Carbon atom reduction also occurs during the formation of Grignard reagents (**79**→**80**). During this process, the Mg atom functions as an electron donor and oxidizes. The process is generically called "oxidative insertion" (it could be called "reductive insertion" considering the carbon atom). During Wurtz reaction (**79**→**43**) there is also a reduction and the



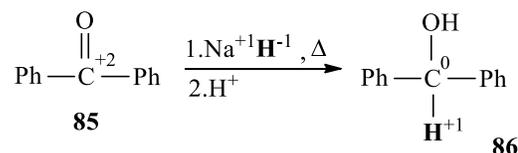
number of hydrogens linked to carbon remain the same. In general, metal is found in organometallic compounds as a cation. In rare cases, however, metal anions may be present [35,36], but in these cases there are no carbon-metal bonds.

Deoxygenation of alcohols via their thiocarbonates **81** to form hydrocarbons **83** is often used in research and is known as the Barton-McCombie reaction (there are many varieties of this process). This reaction requires the use of hydrogen donors such as **82** and follows the radical mechanism. Considering the change of OS of the highlighted carbon atom in substrate **81** and in product **83**, it is perceived that the reaction is a reduction. The same happens in the

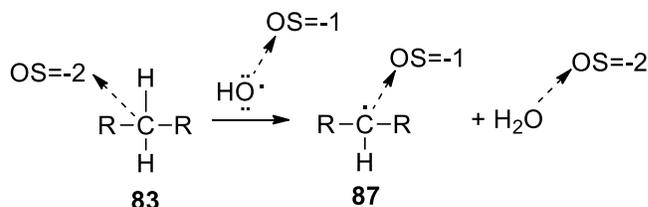


transformation of bis-xanthate **84** to form alkene **69**, using tributyltin hydride **82**.

In *rare* cases, sodium hydride (usually used as a basic agent) can act as a reducer for ketones that do not have hydrogen atoms in the α position and that are not able to form enolate ions, such as benzophenone **85**, and form an alcohol, in this case **86**. [37]

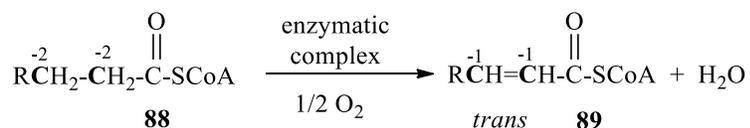


An example of the free radical oxidation via hydrogen atom abstraction by a hydroxyl radical is shown below.

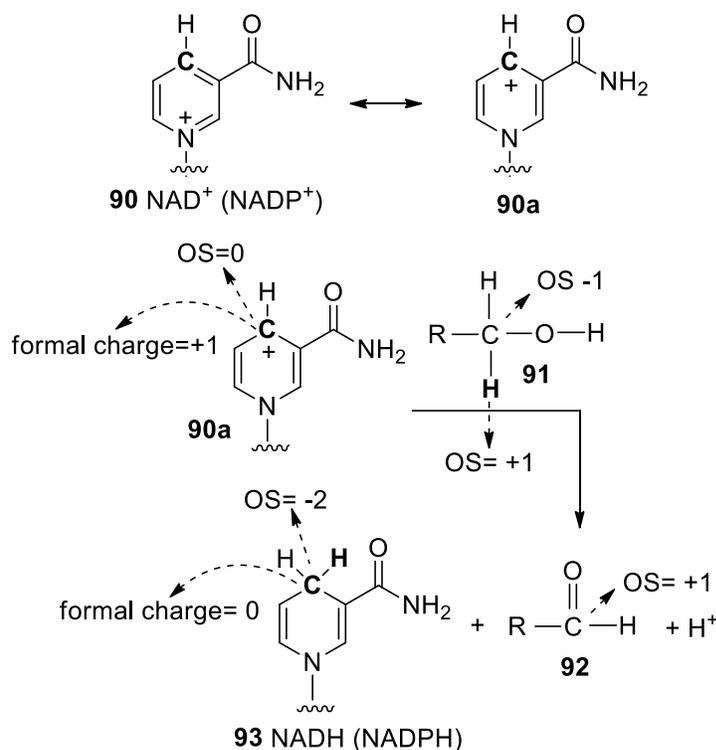


Application Examples

An important catabolism reaction of fatty acids is called β -oxidation. [38-40] This complex enzymatic process transforms fatty acids in their thioester form with coenzyme A (SCoA) **88** into the α,β -unsaturated product **89**. Applying the definition, in which oxidation implies the loss of hydrogen atoms, product **89** is more oxidized than its substrate **88**. Using the formalism of the oxidation state, it is also perceived to be an oxidation, because the change of the OS in **88** and **89** is from -2 to -1.

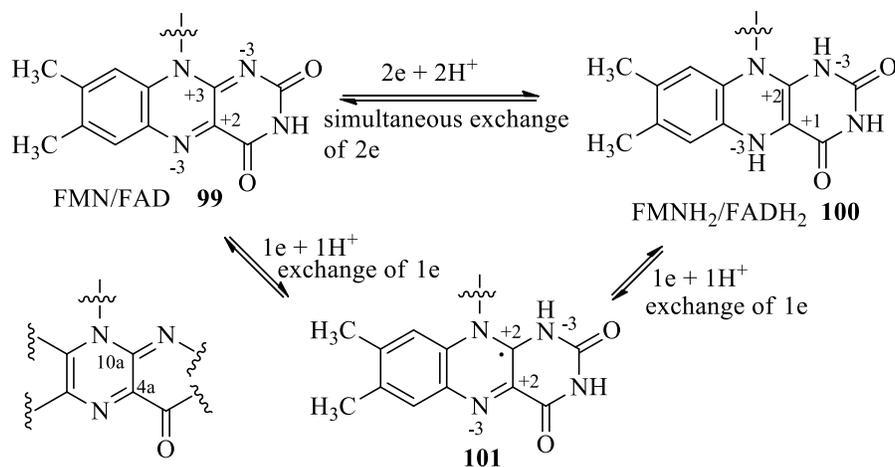


The biological oxidants $\text{NAD}^+(\text{NADP}^+)$ **90** transform substrates **91** into products **92**. [38-40] (Here we ignore stereochemical aspects: which *pro-R* or *pro-S* hydrogen atom is removed in **91** and which is the *Re* or *Si* side of the prochiral **C** atom that is attacked in **90/90a**). It is easier to visualize this reaction using the resonance structure **90a**.



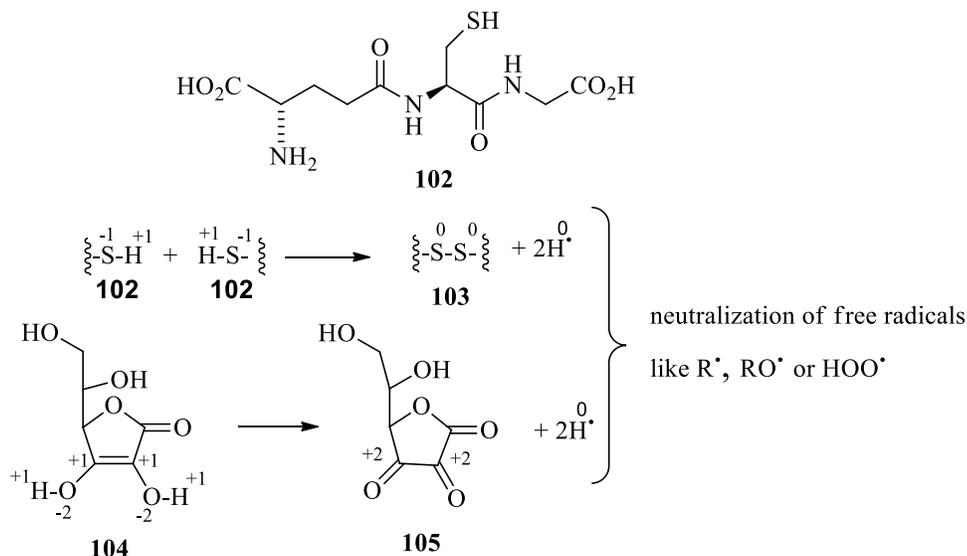
It can be seen that an H^- anion was removed from the molecule of **91** and that the product formed **92**, is more oxidized. This situation has already been considered previously (**49**→**16**). Looking at the changes in the OSs shown above, it could be concluded that the source of the electrons to reduce the atom of **C** in **90a** is the atom of **C** in **91** which shows OS -1 and “lost” two electrons. In fact, it is the atom of **H** in **91** that leaves the molecule of the substrate under the form of hydride. Ironically, the OS of this atom in **91** is +1. **This example shows that the concepts of oxidation states cannot be applied to discuss the mechanisms of reaction.** To amplify this last point, consider the compounds **94-96**, in which an OS of -1 has to be attributed to the chlorine and fluorine atoms and, therefore, it could be thought that the three would function as the donors of the Cl^- or F^- anions. In fact, all three compounds **94-96** react with electron-rich systems, such as enol ether **97**, with total regioselectivity, forming the derivatives **98**, [41,42] with an electrophilic attack in the electron-rich atom.

the neutralization of free radicals (such as the R \cdot , RO \cdot or ROO \cdot) requires the transfer of only one electron. Observing the equilibrium **99** \rightleftharpoons **100**, it can be

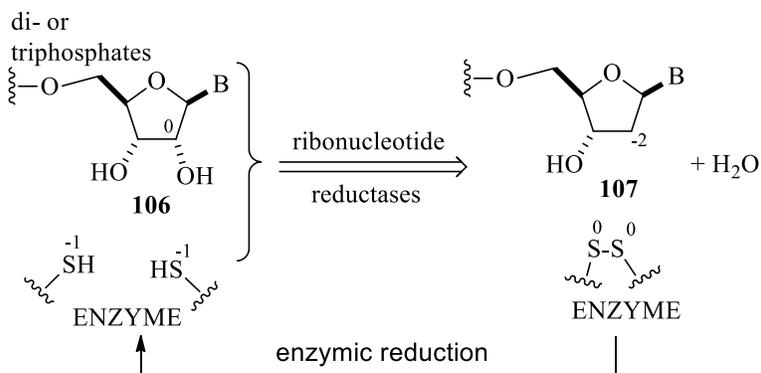


seen that there was a reduction/oxidation of the atoms 10a and 4a, with the exchange of two electrons. However, the equilibria **99** \rightleftharpoons **101** and **101** \rightleftharpoons **100** imply the exchange of one electron per step and only these processes are important during neutralization of free radicals. It should be mentioned that the NAD/NADH and NADP/NADPH systems are capable of exchanging exclusively a pair of electrons. Other reduction/oxidation systems in cells are discussed in the specialized literature. [38-40]

Glutathione **102**, [38-40] a tripeptide that acts as an antioxidant, has an –SH group in its composition. Two –SH groups of two glutathione molecules undergo oxidation to form a disulfide bridge **103** yielding two hydrogen atoms active in neutralization of free radicals formed during the metabolic processes. Likewise, ascorbic acid (vitamin C) **104** acts like a one electron reducer. Similarly, ribonucleotide reductases



[38-40] use their two $-SH$ groups present in one of their active centers to promote the removal of the $-OH$ group from the 2' position of ribonucleotides **106** and form 2'-deoxyribonucleotides **107**, the components of deoxyribonucleic acids. It should be noticed that **107** are more reduced than **106**, hence a name of the enzymes.



CONCLUSIONS

The oxidation state concept applied to organic compounds is useful to show the occurrence of oxidation or reduction sites. Strangely, the use of this concept receives very superficial treatment in the basic texts of Organic Chemistry. In fact, most of the literature consulted does not even

mention about the assessments of the oxidation states in organic compounds. **It is necessary to strongly emphasize the fact that the concept of oxidation state is artificial and cannot be used to rationalize the reactivity of organic compounds, since it does not necessarily reflect the actual distribution of electrons. Additionally, the use of the other than Pauling electronegativity scale, like this of Allen [43-45], furnishes different oxidation states for the compounds containing N-Cl and C-I bonds. Finally, a careful distinction needs to be made when comparing oxidation states and formal charges.**

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