Ahmed Shakir Ph. D. Thesis: ***Persistent free radicals as mediators in oxidation***

Abstract

Free radicals are chemical species that have at least one unpaired electron. This 'free' electron give to the chemical species uncommon properties. The chemistry of free radicals started more than 150 years ago and had an astonishing evolution in the last decades. Organic free radicals are known since the beginning of the 20th century and nowadays are well known as important reactives or intermediates in many physical, chemical or biological processes.

This thesis deals with the study of some free radicals and their possible use as mediators in oxidation processes. The thesis is divided into two main parts, theoretical (literature data) and practical (original experimental data).

First part deals with defining, classifying, synthesis, properties and application of free radicals. Moreover, it highlights most of the nitroxide free radicals. Their applications as effective mediators towards the oxidation of alcohols were taken into account; in a similar way, information about their use in polymerization or redox reactions like dehydrogenation of amines are presented. For all these types of reactions, the oxidation mechanism is established according to literature data.

In the second part of the thesis, original experimental data are presented. Most of them refers to the use of free radicals as intermediates in selective oxidation reactions of alcohols. The study starts with commercially available free radicals of nitroxide or hydrazyl types and then moves towards several types of free mono-, di-, tri- and tetra-radicals, as pure organic compounds.

The next step is their attachment to solid materials, like silica and graphene oxide. Usually, these free radicals are unable to directly oxidize alcohols, therefore a convenient way to generate the corresponding oxoammonium derivative is necessary.

Besides the direct comparison of the properties of such free radicals, a study about the different ways to generate the oxoammonium salts is shown. These were generated using sodium nitrite and acetic acid, sodium hypochlorite, nitrosonium tetrafluoroborate and nitrogen dioxide gas. As alcohols were used benzyl alcohol, 1-phenylethanol, diphenylmethanol, 1-octanol, furfurol and so on.

To improve the oxidation system (in terms of the recovery of the free radical and to ease of the work-up procedures) commercially available silica supported TEMPO has first been used followed by the use of the TEMPO-linked on silica nanoparticles through different linkers. The influence of gold nanoparticles in the oxidation system was also studied.

Finally, TEMPO was covalently grafted onto graphene oxide through an amide bond and the thus obtained material was successfully used as easily recoverable solid catalyst for selective oxidation of some alcohols, using under very mild conditions and oxygen or air as final oxidant. Compounds and materials synthesized were characterized by appropriate means.

It was concluded that oxidations mediated by free radicals represent a viable alternative of the classical ones.