

Abstract

This habilitation thesis presents the main results obtained by the author after his Ph.D thesis (1997) till now (2012). The general subject hold throughout the thesis is the organic chemistry of the stable free radicals, with an emphasis on the stable free radicals of hydrazyl or nitroxide types. The thesis is structured into three sections, as has been requested by the general information rules: thus, the first part describes the scientific work already achieved, proved by published papers; the second part is about new directions of scientific and academic development; and finally, in the third part are shown the references used in the first two parts.

In the first part, the opening chapter is dedicated to a general introduction in organic free radical chemistry, their usual and most known classification, elementary notions about their stability and techniques used for detection. The readers will understand what commonly means the term of free radical and why they are important in any science, and also what is the unusual property that detaches them from all other known compounds.

Following the introductory section, the next chapter deals with the synthesis of the most known types of mono- and poly-radicals, such are the organic stable radicals of hydrazyl type, nitroxide type, nitronyl-nitroxide type and imino-nitroxide type. All these are presented in separate sections, highlighting their methods of synthesis and the chemical structure of the new compounds thus obtained. This chapter included also the synthesis of some di-, tri-, and tetra-radicals, compounds with several cumulative properties, of high interest in materials science (for example, in single magnet molecules research).

The next chapter is dedicated to the properties of the newly synthesized organic stable free (poly)radicals. Their electron resonance spectra (as this is the distinctive method of evidencing, analysis and characterization of the free radicals) are presented and discussed in details, as well as other properties of interest, such are acid-base, redox, hydrophobicity, and so on.

Between the all types of stable free radicals showed, hydrazyls ones are quite important, due to their multifunctional behavior. Depending on the molecular structure, these can be used as sensors and probes in a myriad of physical and chemical processes.

Organic stable hydrazyl free radicals can be also used as generators of other short-lived free radicals, as pH sensors, as probes for liquid crystals, as scavengers of unstable free radicals (including reactive oxygen species), and as probes for free radicals formed in cigarette smoke. Detailed information obtained using specific synthesized hydrazyl free radicals are already published and presented during several sub-chapters.

Materials chemistry and free radicals is another chapter of the first section. In this chapter, several organic or inorganic types of materials were used in conjunction with organic free radicals chemistry. Thus, gold nanoparticles, bulk silica or silica nanoparticles, hybrid gold-silica nanoparticles, and cellulose materials were used in different combination with organic stable free radicals, mainly of nitroxide type.

Most of the newly synthesized free radicals were used as probes or labels (markers) to study different physical and chemical processes, mainly following one of the next two ways. In the first one, a straightway, the free radicals are in contact with the desired materials just by simple mixing, and the interaction of these was studied by different means. In the second way, the free radical is covalently attached to the solid material and the interactions studied. A tremendous number of measurements can be performed, leading to a huge amount of useful information; detailed data are therefore presented and discussed in different sub-chapters, for a particular process.

After the first part of the habilitation thesis (which presents and discuss some of the already published results), in the second part (which is about the new directions of scientific and academic development) are presented several paths of further development; some of them can be regarded as a natural extension of the previous work, and some others tries to push-up new ideas related to organic free radical chemistry. Thus, therein are shown chemical structures of some new (poly)radicals meant to be obtained and characterized, and a discussion of their expected properties; in materials chemistry several guidelines are shown, related to previous work; as well, new interesting directions, not related with previous papers in free radicals chemistry, but keeping the same general subject, are also revealed.

The last part of the habilitation thesis consists in the references section; all the bibliographic data that appears throughout the main text is compiled here, with an emphasis (in blue) of the author published scientific papers.

Rezumat

Teza de abilitare prezinta principalele rezultate obtinute de autor, dupa sustinerea publica a doctoratului in chimie (1997), si pana in prezent (2012). Tematica generala a tezei o reprezinta chimia radicalilor liberi de natura organica, in care o pondere mai mare o au radicalii liberi stabili de tip hidrazil si nitroxid. Teza este structurata in trei parti, conform cerintelor impuse; prima parte descrie rezultatele stiintifice obtinute, sustinute de lucrarile publicate; a doua parte descrie directiile noi de cercetare si dezvoltare academica, propuse de autor; ultima parte contine referintele bibliografice, comune celor doua parti.

In prima parte, capitolul introductiv este dedicat initierii in chimia radicalilor liberi, incluzand clasificarea acestora, notiuni elementare privind stabilitatea lor, tehnici uzuale de detectie. Cititorul va fi familiarizat cu termenul de radical liber, importanta acestor compusi in stiinta, proprietatile deosebite care ii separa de toti ceilalti reactivi chimici.

Urmatorul capitol prezinta modalitatile de sinteza a celor mai cunoscute tipuri de mono- si poli-radicali, asa cum sunt cei de tip hidrazil, nitroxid, nitronil-nitroxid si imino-nitroxid. Toti acestia sunt prezentati in sectiuni separate, punandu-se in evidenta metodele lor de obtinere si caracteristicile structurale. Capitolul include si sinteza unor di-, tri- si tetra-radicali, compusi cu proprietati cumulative, de mare interes in stiinta materialelor (in domeniul magnetilor moleculari).

Proprietatile fizico-chimice ale radicalilor prezentati sunt abordate in capitolul urmator. Rezonanta electronica de spin (RES) este prezentata ca fiind tehnica distinctiva utilizata pentru evidentierea, analiza si caracterizarea radicalilor liberi. Dintre diversele proprietati de interes ale acestor compusi, sunt prezentate cele mai cunoscute, de tip acido-bazic, redox, hidrofobicitate, etc.

Radicalii liberi de tip hidrazil prezinta o importanta majora, datorita multifunctionalitatii lor. In functie de structura moleculara, acestia pot fi folositi ca sensori, markeri sau probe intr-o multime de procese fizice sau chimice.

De asemenea, radicalii liberi stabili de tip hidrazili pot fi folositi ca generatori de alti radicali liberi cu viata scurta (instabili), ca senzori de pH, ca probe pentru cristale lichide sau pentru radicalii formati in fumul de tigara, sau ca si captatori de alte specii instabile sau foarte reactive (specii reactive ale oxigenului). Informatii detaliate despre utilizarile specifice ale acestora sunt prezentate in lucrarile publicate si in prezenta teza in cateva subcapitole.

Un alt capitol al primei parti este denumit radicali liberi in chimia materialelor. Aici sunt prezentate cateva tipuri de materiale, organice sau anorganice, utilizate in prezenta radicalilor liberi. Nanoparticule de aur, de silice, mixte, sau celuloza au fost folosite ca materiale de studiu in diferite combinatii cu radicali de tip nitroxid.

Marea majoritate a radicalilor liberi sintetizati de autor au fost folositi practic in studiul unor procese fizico-chimice, utilizand in principal doua cai. In prima cale, cea directa, radicalii liberi vin in contact cu materialele studiate prin simpla amestecare, iar interactia este studiata prin diferite tehnici specifice. In cea de a doua cale, radicalii liberi stabili sunt legati covalent

de materialul studiat. Numeroase masuratori pot fi astfel facute, care pot conduce la o cantitate uriasa de informatie utila.

Partea a doua a tezei de abilitare prezinta directiile noi de cercetare stiintifica si dezvoltare academica; unele dintre acestea pot fi privite ca o extindere naturale a subiectelor discutate anterior, iar altele incearca sa evidentieze idei noi in chimia radicalilor liberi. Astfel, sunt prezentate structuri chimice ale unor noi mono- si poli-radicali stabili, discutandu-se posibilele lor aplicatii si proprietati. De asemenea, in domeniul materialelor sunt aratate cateva noi directii interesante de studiu.

Ultima parte a tezei o reprezinta bibliografia, comuna celor doua parti anterioare, unde cu [albastru](#) sunt puse in evidenta titlurile publicate de autor.