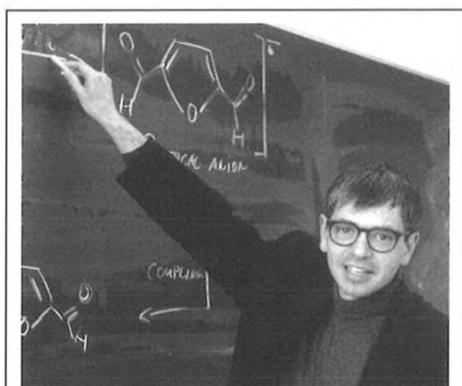


Radicals and Radical Ions in Chemistry, Life and Material Sciences

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Abstract. Radicals are almost everywhere. This compilation shows how and where these short-lived species are generated and which methods are utilized for their investigation in our laboratory. Three examples from the fields of supramolecular chemistry, pharmacologically active compounds, and material science are outlined.



Georg Gescheidt was born 1958; he studied chemistry in Freiburg im Breisgau (Germany) where he obtained his masters degree. His dissertation was carried out in the group of F. Gerson (Basel, 1988). After two years of editorial work he returned to the university and obtained his habilitation in 1996.

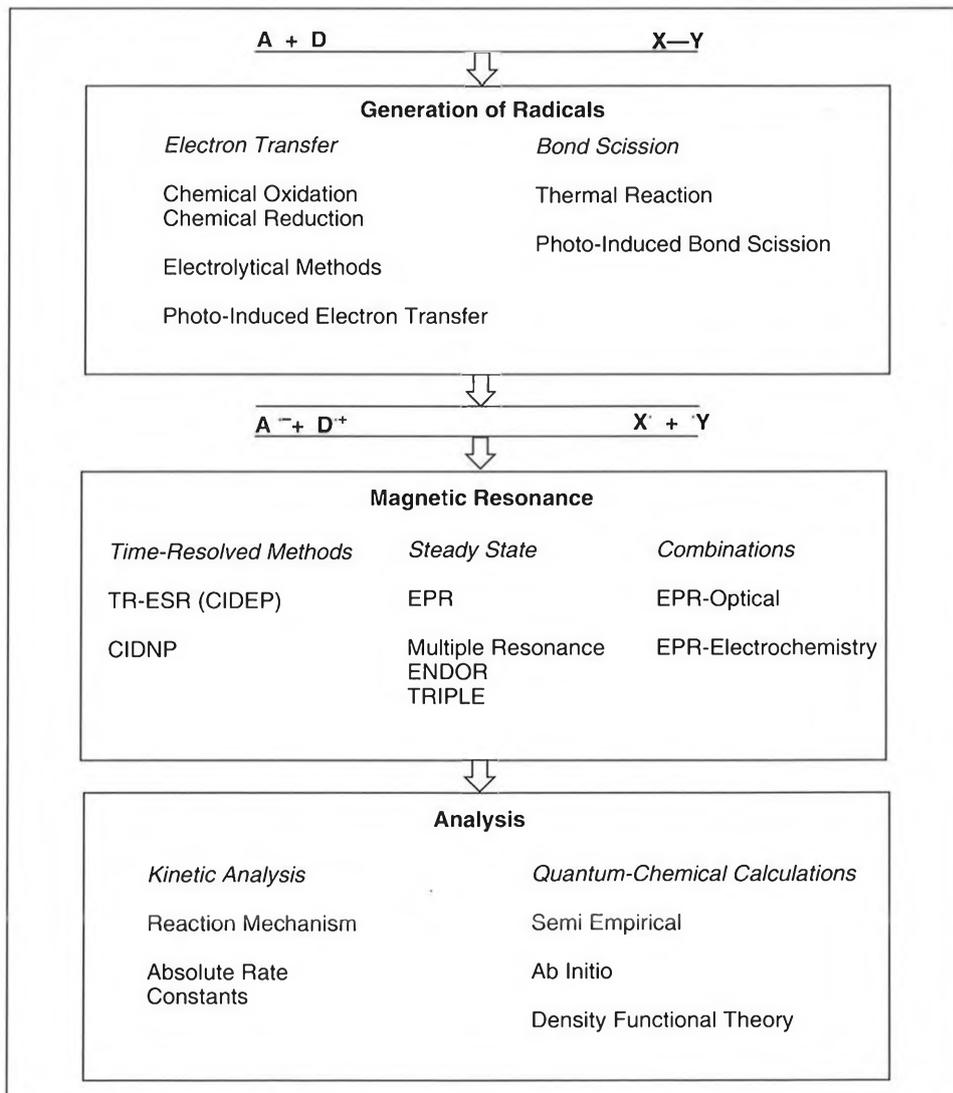
Introduction

Electron transfer and the scission of a covalent bond are the simplest conceivable chemical transformations. Such reaction steps can be found in an almost unlimited number of molecular reactions, *e.g.*, in 'classical chemical reactions' like the acyloin condensation, 'hole-catalysed' pericyclic reactions [1], DNA scission [2], or curing processes [3]. In the first step, both reactions lead to the formation of

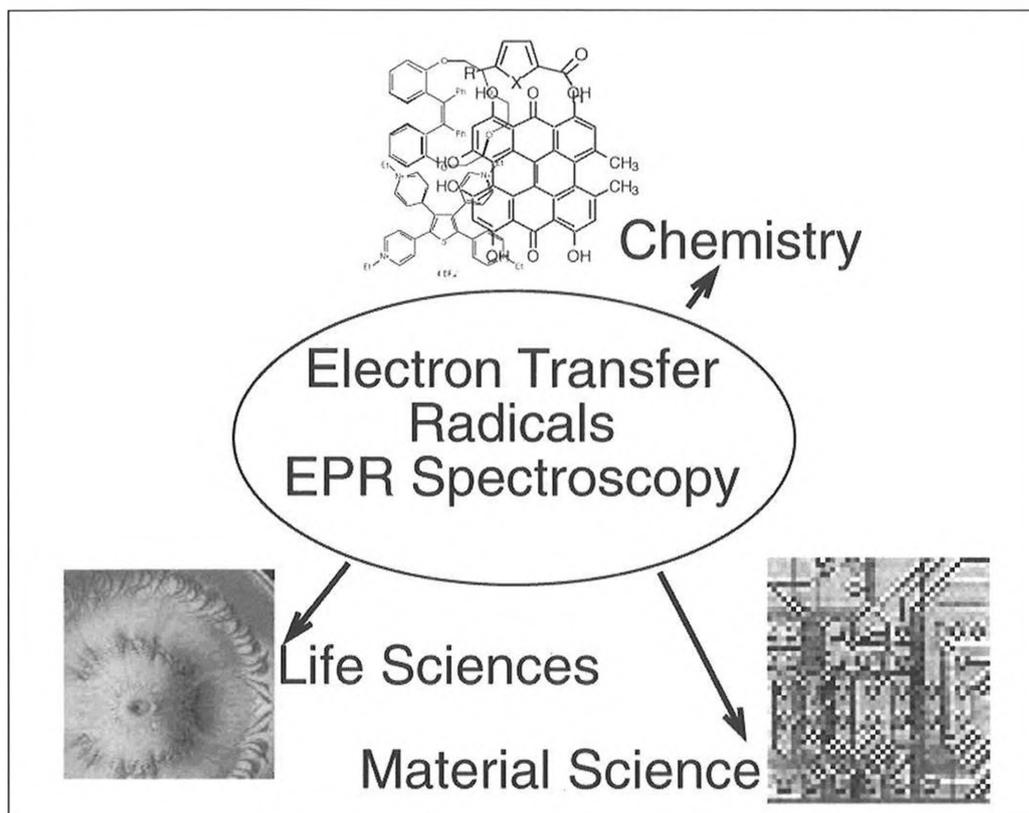
Scheme 1



Scheme 2



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Scheme 3

species with one unpaired electron (*Scheme 1*; starting from closed-shell molecules).

Electron transfer between acceptor (A) and donor (D) leads to the formation of a radical anion/radical cation pair (A^-/D^+), whereas bond scission produces two neutral radicals ($X\cdot, Y\cdot$).

Experimental Techniques

To achieve a comprehensive picture and understanding of these reactive species, they are generated by appropriate methods and inspected by magnetic resonance spectroscopy in the time-resolved regime (ns time range) or at steady-state conditions and by combined simultaneous spectroscopic techniques [4]. The experimental results are then compared with theoretical calculations performed at various levels of theory. Details are given in *Scheme 2*.

Some Projects

According to the essential character of the radical-forming reactions (*Scheme 3*), we have been investigating a vast palette of questions.

i) Electron-Transfer Properties of Pharmacologically Active Quinones

In this project, we inspect the relationship between the structure of one-electron

reduced derivatives of anthraquinone-derived compounds (e.g., anthracyclines or hypericin, present in *St. John's wort*) [5] and the antiviral activity of such compounds.

ii) Supramolecular Effects on the Reactivity of Organic Radical Ions

The influence of association phenomena on coupling reactions of aldehydes and the efficiency of crown-ether complexation is studied [6].

iii) Properties of Photoinitiators for Radical Polymerisations

We investigate, predominately by time-resolved methods, the kinetics of the addition of alkenes to initiator radicals. Moreover, models for structure-reactivity relationships are being developed [7].

iv) Calculations of Isotropic Hyperfine Coupling Constants

We have been evaluating quantum-chemical methods for the identification of organic radicals [8].

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