OC2

Radicals & Polymerisation
–
Introduction to Radicals

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Introduction to Radicals

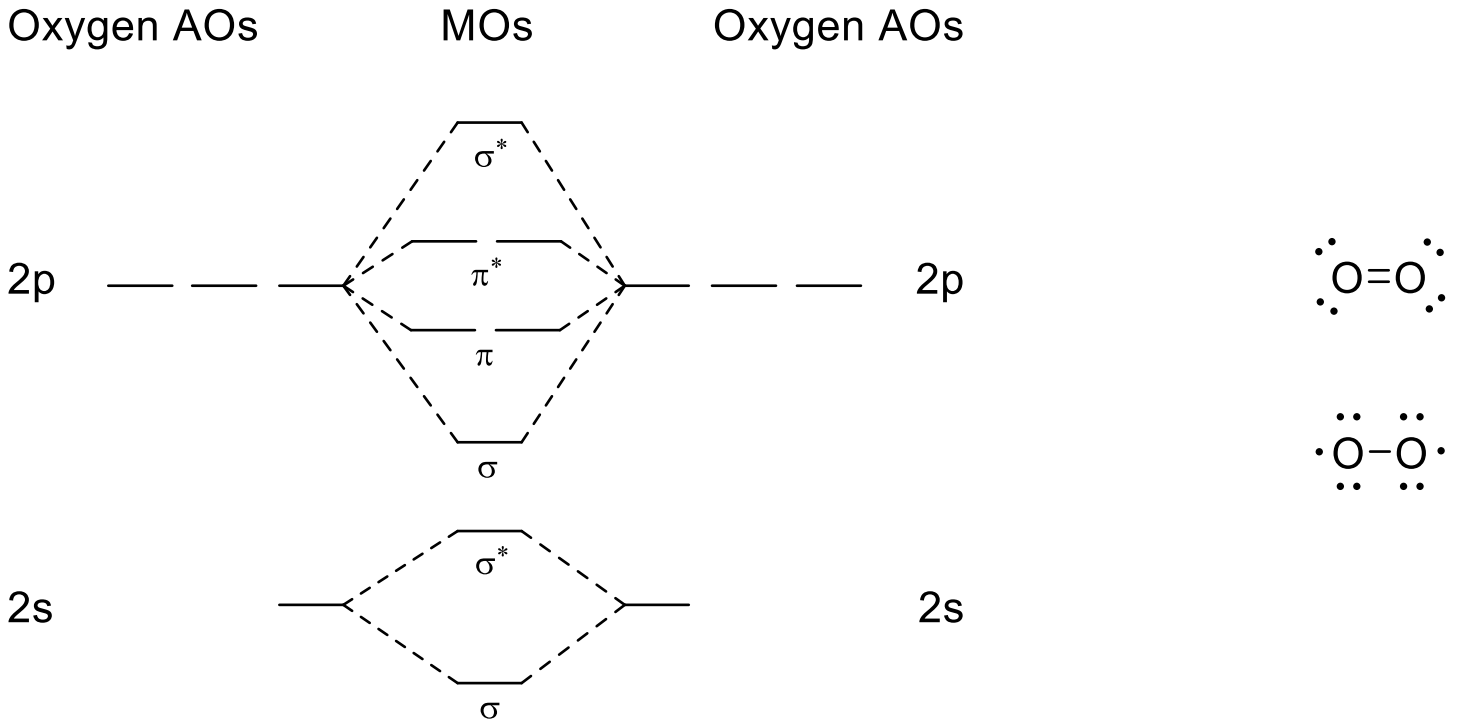
*"Think of **radicals as smash-and grab raiders**. They pick the first shop that catches their eye, smash the window, and run off with a handful of jewellery from the front of the display.*

***Ions in solution are stealthy burglars**. They scan all the houses on the street, choose the most vulnerable, and then carefully gain entry to the room that they know contains the priceless oil painting."*

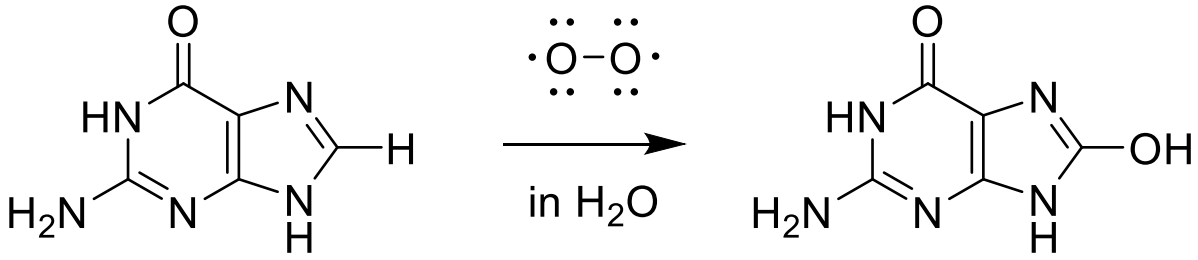
Organic Chemistry, by Clayden, Greevs, Warren, Wothers, OUP 2nd Edition, p. 1033

Introduction to Radicals

Radicals (such as O_2) are involved in DNA damage and other cellular degradation processes.



Radicals enable powerful chemical transformations:

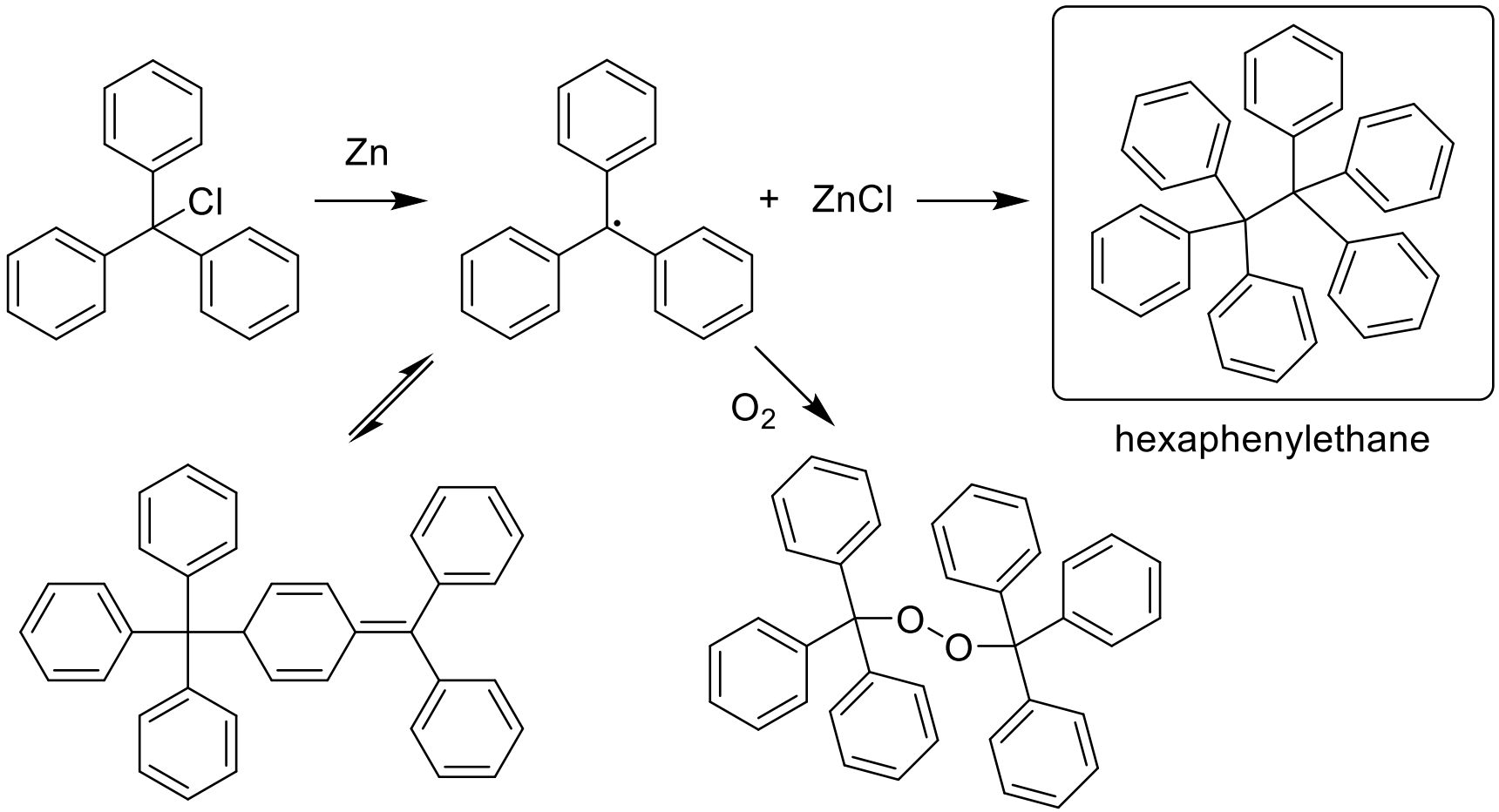


Guanine

8-hydroxy guanine

- Molecular oxygen (O_2) is a diradical, with an oxygen-oxygen bond order = 1 (i.e., a single bond) and one unpaired electron on each oxygen atom (Lewis Theory gets this wrong).
- Guanine (G, Gua) is one of the four main nucleobases found in the nucleic acids DNA and RNA, the others being adenine, cytosine, and thymine (uracil in RNA).

“On Trivalent Carbon”



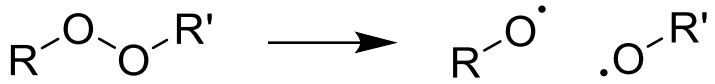
hexaphenylethane

Moses Gomberg (Feb 8, 1866 – Feb 12, 1947) credited for the “Discovery of Organic Free Radicals” during his tenure at the University of Michigan.

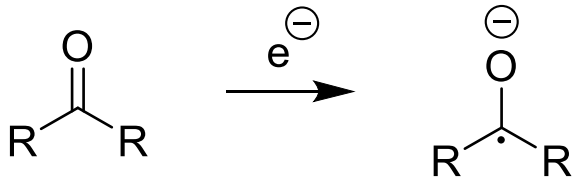
“This work will be continued and I wish to reserve the field for myself.” – M. Gomberg, 1900

Radical Formation *via*

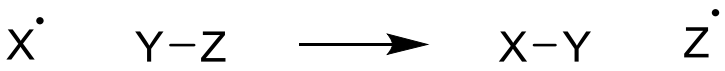
(1) **Homolysis** of weak σ-bonds



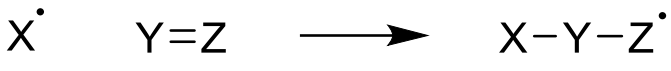
(2) **Electron transfer** (reduction)



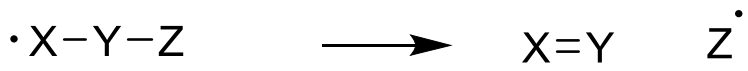
(3) **Substitution** (**2**nd order **H**omolytic **S**ubstitution or S_H2)



(4) **Addition**

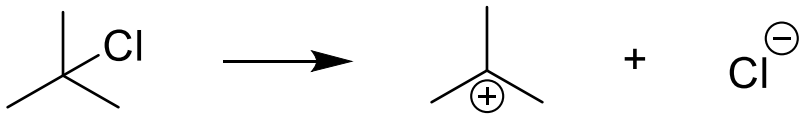


(5) **Elimination**



Heterolysis and Homolysis

Heterolysis: bonds break and one atom gets both bonding electrons; products are **ions**.



8 electrons in outer shell

- **Heterolytic cleavage:** two electrons of σ-bond go the same way (e.g. S_N2)
- **Curly arrows** move two bonding e^- (bonds broken/formed) and show where e^- come from (C^+), and where they go (A^-)

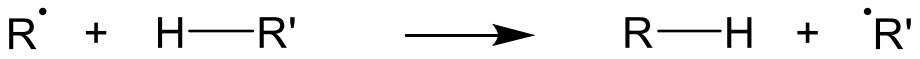
Homolysis: bonds break and the atoms get one bonding electron each; products are **radicals**.

7 electrons in outer shell each

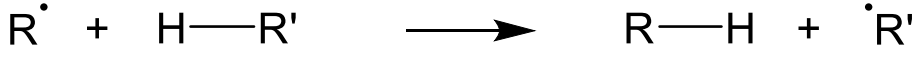
NOTE: Radicals are neutral species, so **changes in solvent polarity have little effect** on rate.

- **Homolytic cleavage:** two electrons of σ-bond go opposite ways
- **'Fish-hook' arrows** moving one electron only

Two ways of drawing a radical mechanism:



or



NOTE:
$Cl^{\bullet}$ – single unpaired electron is denoted by a dot. $Cl^{\bullet}$ radical still has another three pairs of electrons that are not shown.

What’s next?

Radical Formation