SELECTED CHAPTERS OF PHYSICAL CHEMISTRY OF SOLUTIONS

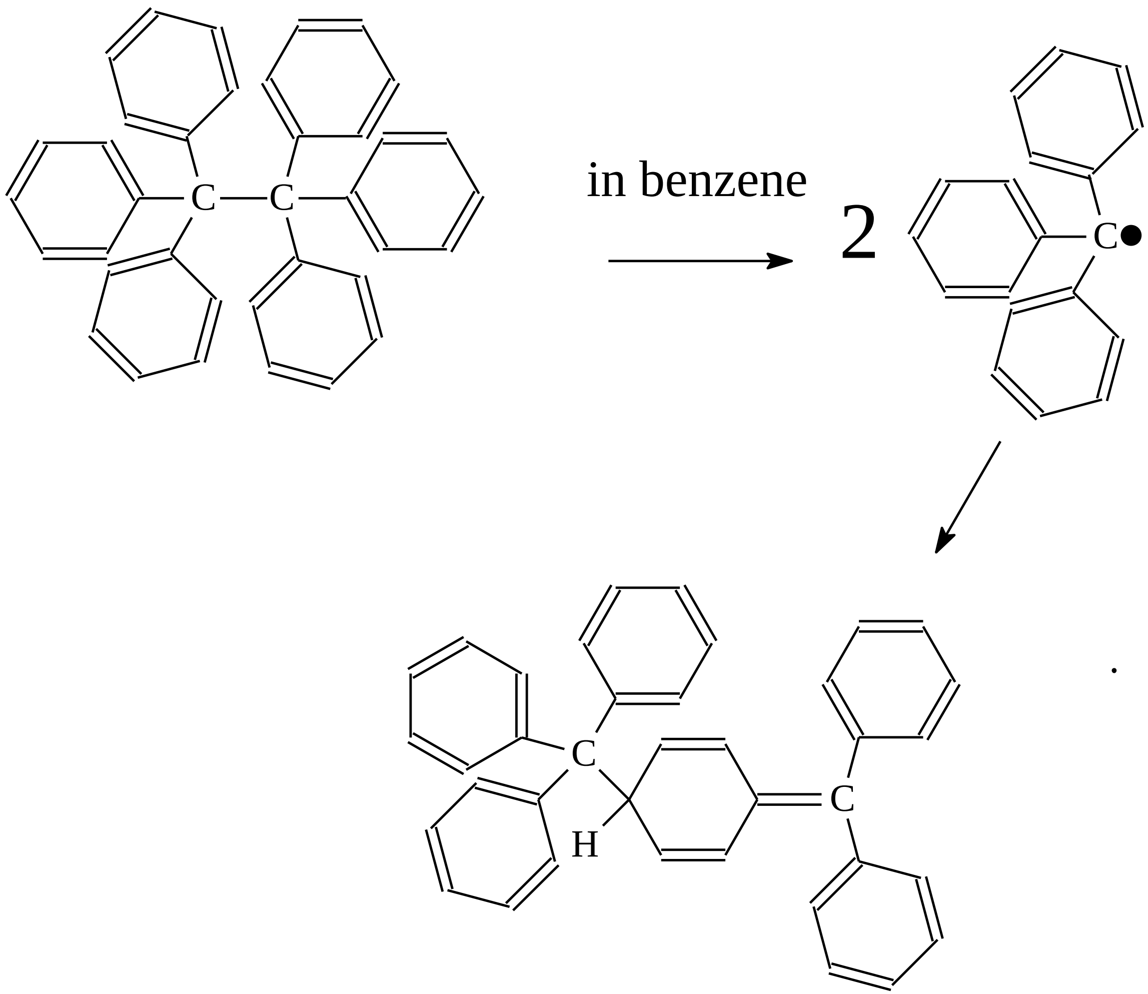
Free Radicals

Species with unpaired electrons

Discovery of the free radicals
M. Gomberg, 1900

Species with unpaired electrons

A cryoscopic study:



Yellow color

Methods of preparation

$$Ph_3C^\bullet + PhCH_3 \rightarrow Ph_3CH + PhCH_2^\bullet$$

in water:

$$Ph_3CH \xrightarrow{HO^-} Ph_3C^- \xrightarrow{[O]} Ph_3C^\bullet$$

$$Ph_3CCl \xrightarrow{Ag} Ph_3C^\bullet + AgCl$$

Free radicals are paramagnetic.

They are detected via the ESR (or EPR) method

Different ways of free radicals formation

Photolysis, thermolysis

$$Ph_2C{=}O \xrightarrow{h\nu} Ph_2C{=}O^* \rightarrow Ph_2C^{\bullet} - O^{\bullet}$$

singlet triplet

$$Ph_2C^{\bullet} - O^{\bullet} + H(CH_3)_2CPh \rightarrow Ph_2C^{\bullet} - OH + {}^{\bullet}C(CH_3)_2Ph$$

cumene

Examples of homolytic dissociation

G. Razuvaev, V. Ipatiev:

$$Hg(CH_3)_2 \xrightarrow{\text{in } CCl_4} CH_3Hg^\bullet + {}^\bullet CH_3$$

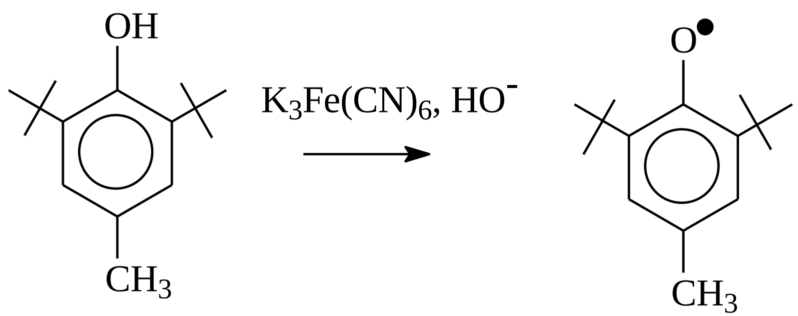
$$^\bullet CH_3 + CCl_4 \rightarrow CH_3Cl + CCl_3^\bullet$$

$$CH_3Hg^\bullet + CCl_4 \rightarrow CH_3HgCl + CCl_3^\bullet$$

$$2CCl_3^\bullet \rightarrow C_2Cl_6$$

Chemical oxidation

Two-phase reaction (water/benzene; Cook)



Other inorganic oxidants: PbO_2; Ag^+; Ce^{4+}

$$ArO^- + Ce^{4+} \rightarrow ArO^\bullet + Ce^{3+}$$

Electrochemical oxidation

$$RCOO^- \xrightarrow{-e} CO_2 + R^\bullet \rightarrow \frac{1}{2} R_2$$

Reduction

$$Ph_3C^+ + V^{2+} \rightarrow Ph_3C^\bullet + V^{3+}$$

The Fenton reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + HO^-$$

Al/Ni alloy:

$$C_{60} + \text{Al/Ni alloy} \xrightarrow{\text{in tetrahydrofurane}} C_{60}^{\bullet-}$$

$$C_{60}^{\bullet-} + O_2 \xrightarrow{\text{in water}} C_{60}\ \text{(colloid solution)}$$

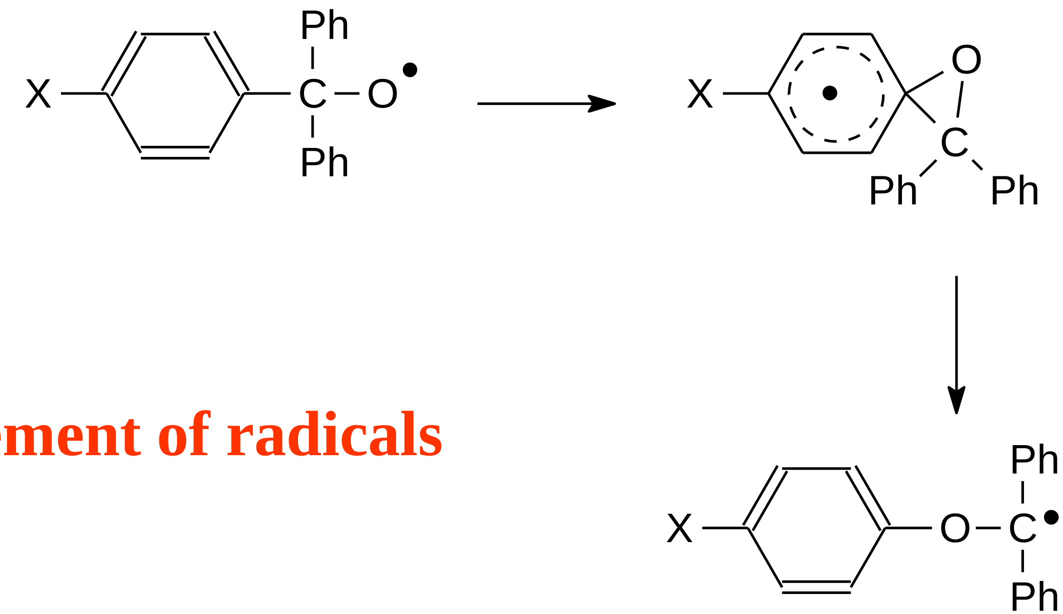
Reduction

Other reductors: K or Na amalgam

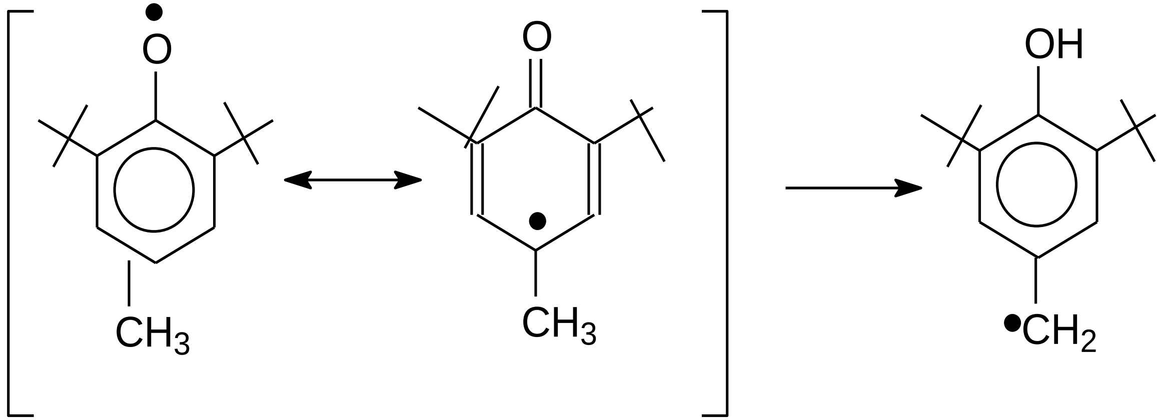
Electrochemical reduction

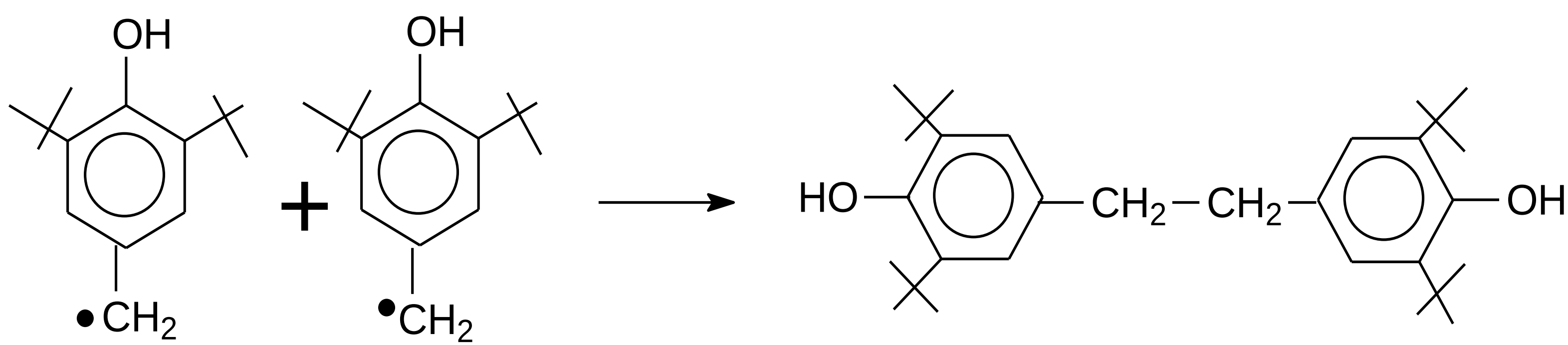
$$R \xrightarrow{e^-} R^{\bullet -} \xrightarrow{e^-} R^{2-}$$

Some reactions of radicals

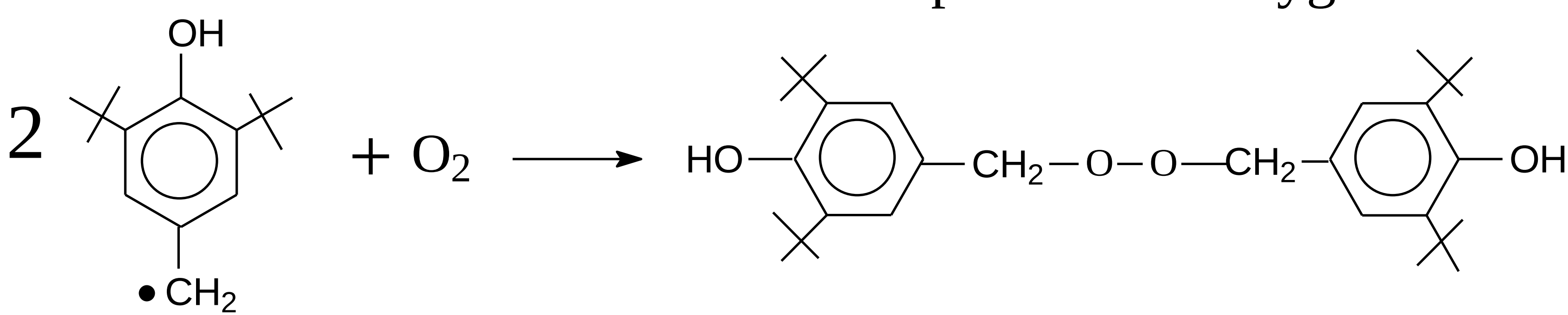


Rearrangement of radicals



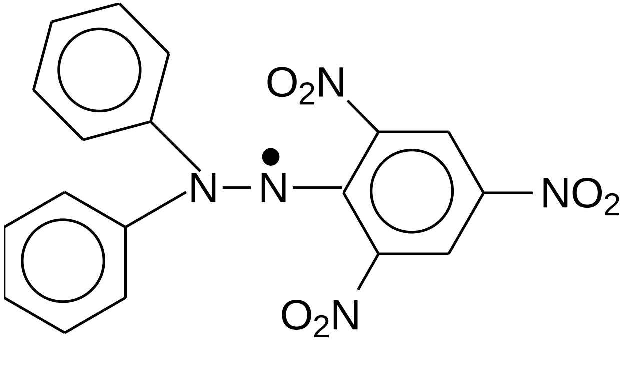


Dimerization in the presence of oxygen

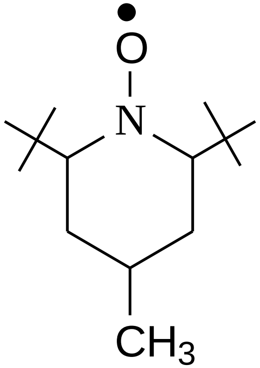


Stable radicals

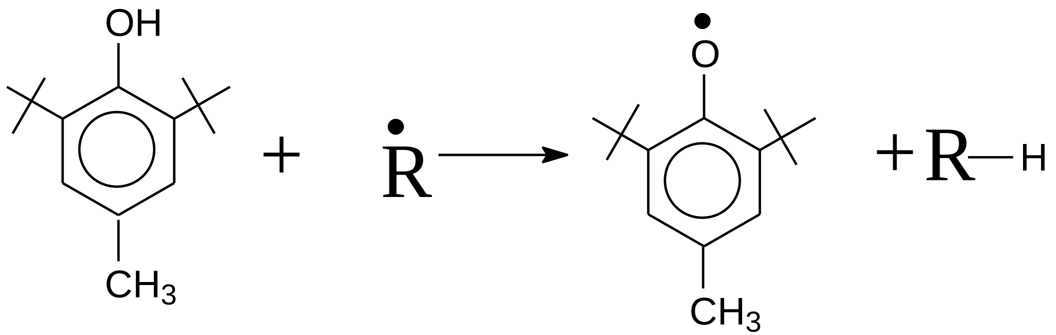
1,1-diphenyl-2-picrilhydrazine



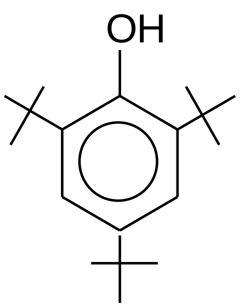
Paramagnetic stain



Radical scavengers

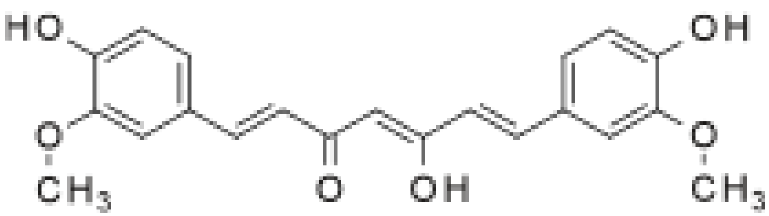


Ionol

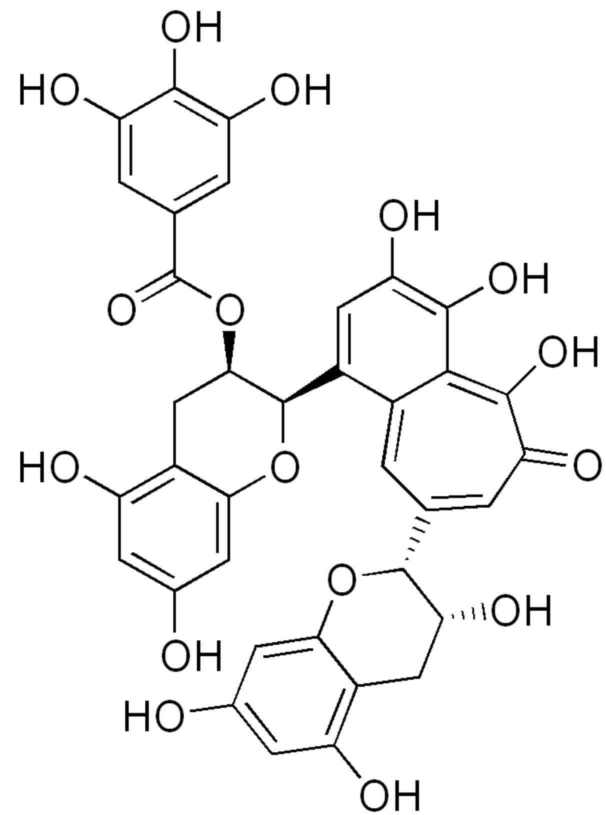


Antioxidants. Polyphenols

Polyphenols arefound in plants and have healing properties



Curcumin

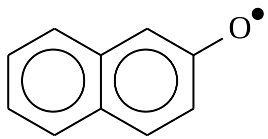


Theaflavin-3-gallate, a plant-derived polyphenol, an ester of gallic acid and a theaflavin core

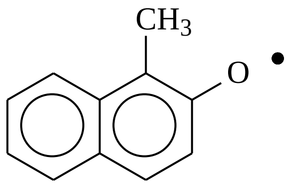
Factors that determine the stability of radicals

$\tau_{1/2}$

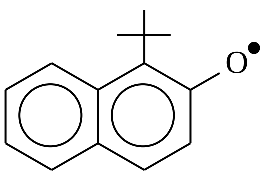
(Conjugation and steric hindrance)



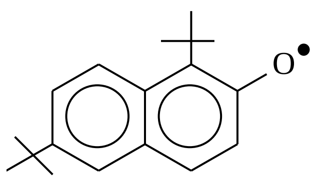
< 2 s; 5 ^{o}C



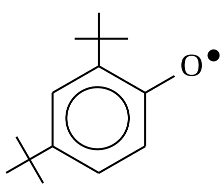
10 s; 5 ^{o}C



38.5 h; 20 ^{o}C



42 h; 20 ^{o}C



20 s

General scheme of oxidation of organic matter. Inhibition of oxidation processes

$(0)\ RH \xrightarrow{O_2} R^{\bullet}$ (origin of chains)

$(1)\ R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$

$(2)\ ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$ (continuation of chains)

$(3)\ ROOH \rightarrow RO^{\bullet} + HO^{\bullet}$ (branching degenertion)

$(4)\ R^{\bullet} + R^{\bullet} \rightarrow R - R$ (break of chains)

$(5)\ ROO^{\bullet} + R^{\bullet} \rightarrow ROOR$ (break of chains)

$(6)\ ROO^{\bullet} + ROO^{\bullet} \rightarrow ROH + R^{/}COR + O_2$ (break of chains)

$(7)\ ROO^{\bullet} + InH \rightarrow ROOH + In^{\bullet}$ (inhibition)

$(8)\ In^{\bullet} + In^{\bullet} \rightarrow In - In$ (inhibition)

$(9)\ In^{\bullet} + ROO^{\bullet} \rightarrow InOOR$ (inhibition)