

OC2

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Radicals & Polymerisation

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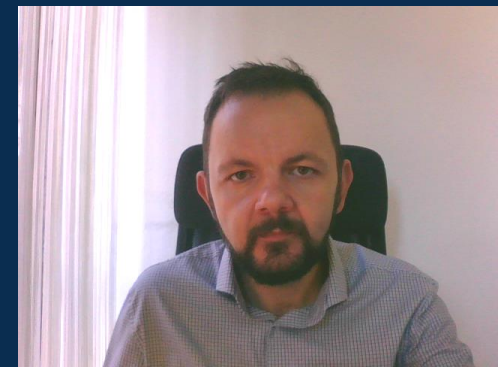
Radical Formation

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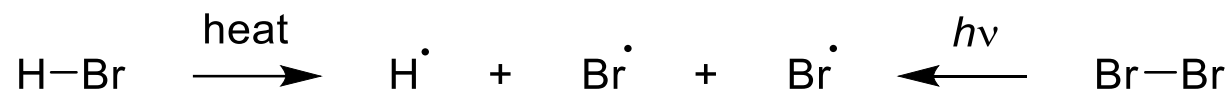
@mjbojdys



(1) Homolysis

Why not form Br• by heating HBr?

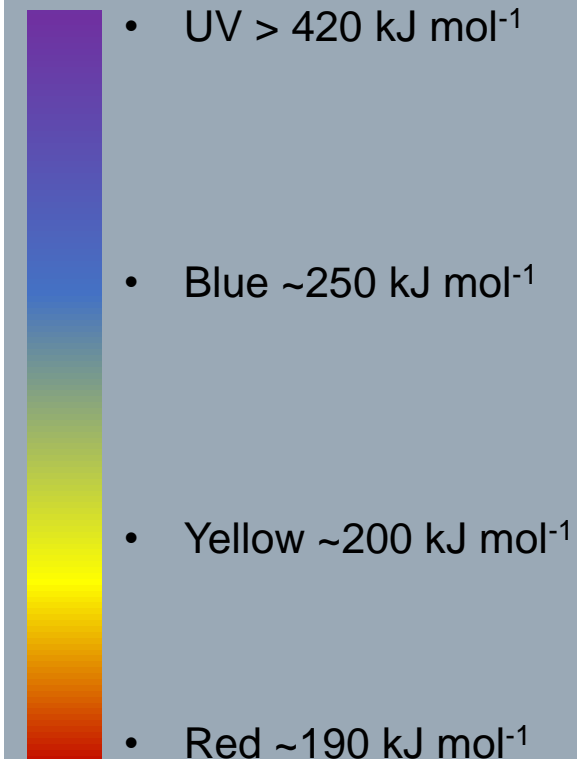
Or by shining light on Br₂?



Key to understanding which bonds cleave homolytically is **bond strength**

ΔG for homolytic cleavage (kJ mol⁻¹)

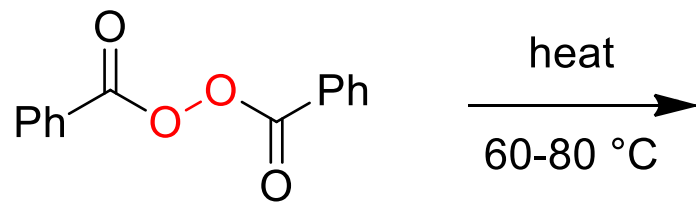
RO-OR	Br-Br	H-OR	H-Br	CH ₃ -OR	CH ₃ -Br
151	192	498	366	383	293



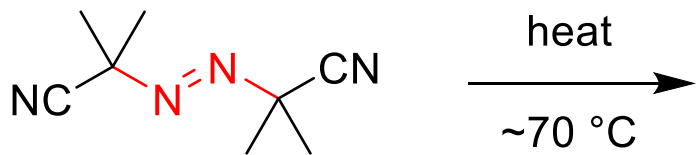
UV will decompose many organic compounds (incl. pigments in paintings, DNA in skin, etc.)

(1) Homolysis

Formation of radicals by **homolysis** of weak σ -bonds



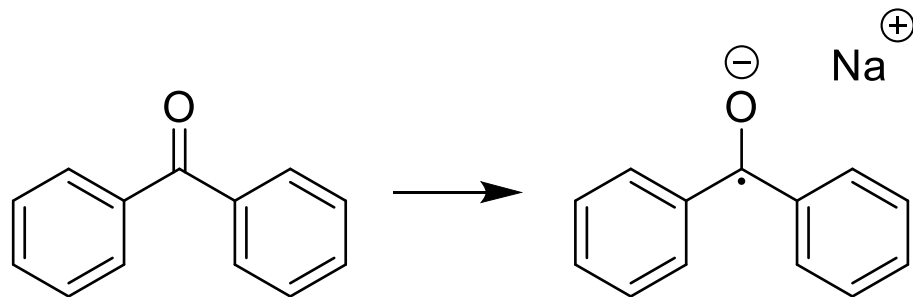
dibenzoyl peroxide



AIBN
Azo(bis)IsoButyroNitrile

(2) Electron Transfer

Reduction, i.e. transfer of a single electron from e.g. a group I metal to a molecule



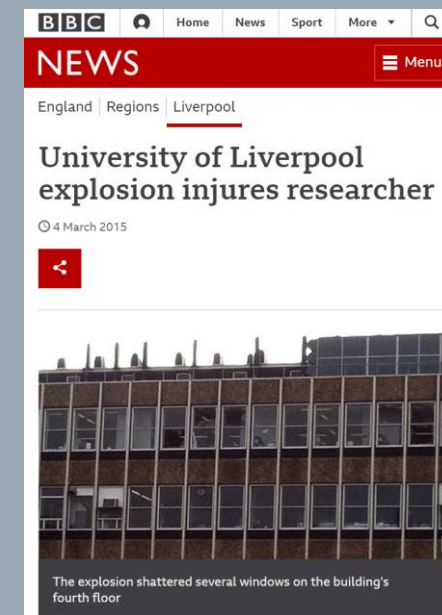
vivid blue solution due to “solvated electrons” (i.e. formation of radical anion)

Solution of sodium in benzophenone ketyl radicals



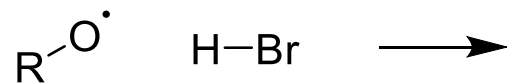
used for the preparation of anhydrous solvents (< 10 ppm H₂O)

CAUTION: conc. dispersion/solution of Na, ketyl radicals and solvent may lead to explosions!

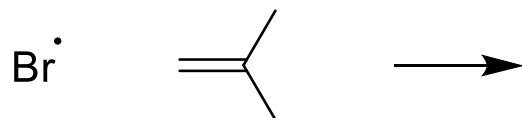


Radicals formed from other Radicals by

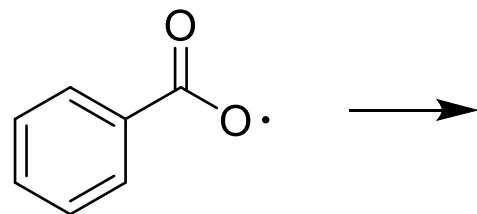
(3) **Substitution** (sometimes called **Abstraction**)



(4) **Addition**



(5) **Elimination** (Homolysis)



What's next?

Radical Stability, Selectivity and Radical Chain Reactions

