Question #61073 – Chemistry – Organic Chemistry

Question:

List the various methods of generation of free radicals. Discuss in detail various redox sources of free radical generation.

Answer:

Methods of generation of free radicals

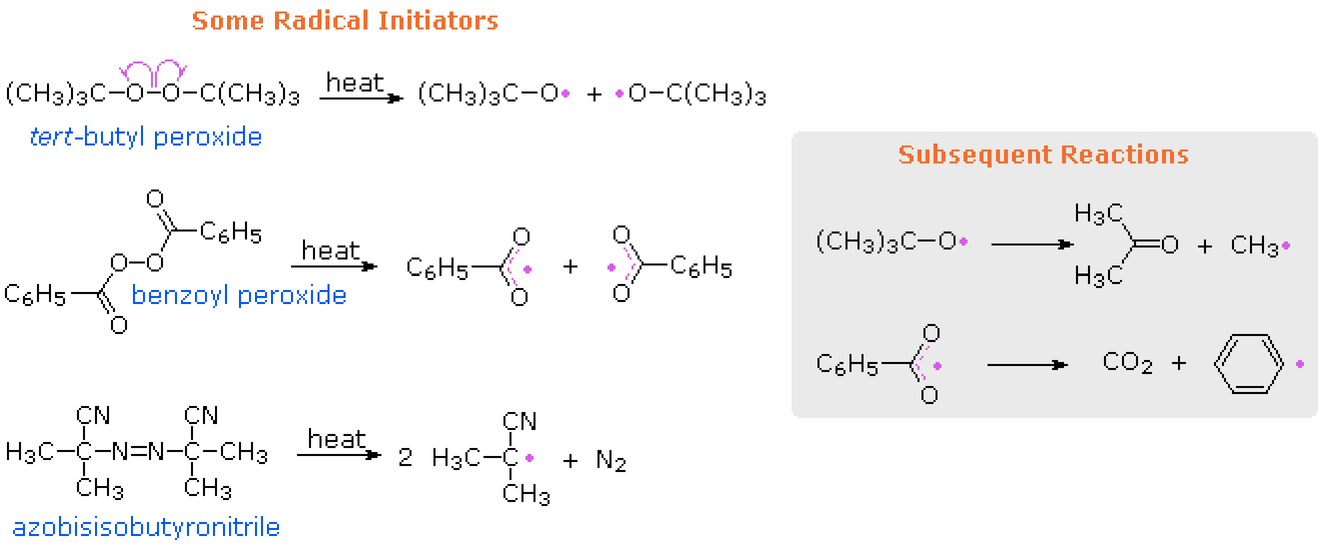
Thermal Cracking

At temperatures greater than 500º C, and in the absence of oxygen, mixtures of high molecular weight alkanes break down into smaller alkane and alkene fragments. This *cracking process* is important in the refining of crude petroleum because of the demand for lower boiling gasoline fractions. Free radicals, produced by homolysis of C–C bonds, are known to be intermediates in these transformations. Studies of model alkanes have shown that highly substituted C–C bonds undergo homolysis more readily than do unbranched alkanes. In practice, catalysts are used to lower effective cracking temperatures.

Homolysis of Peroxides and Azo Compounds

In contrast to stronger C–C and C–H bonds, the very weak O–O bonds of peroxides are cleaved at relatively low temperatures (80 to 150 ºC), as shown in the following equations. The resulting oxy radicals may then initiate other reactions, or may decompose to carbon radicals, as noted in the shaded box. The most commonly used peroxide initiators are depicted in the first two equations.

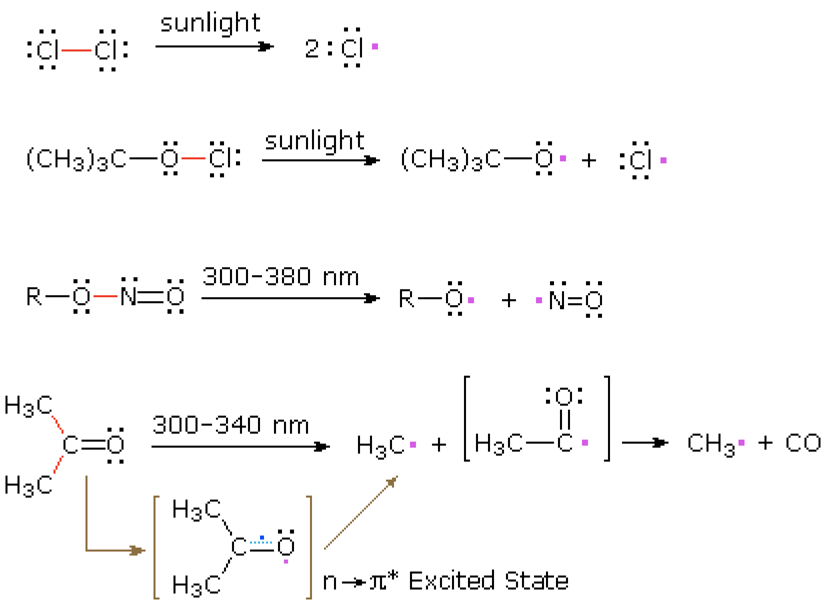
Organic azo compounds (R–N=N–R) are also heat sensitive, decomposing to alkyl radicals and nitrogen. Azobisisobutyronitrile (AIBN) is the most widely used radical initiator of this kind, decomposing slightly faster than benzoyl peroxide at 70 to 80 ºC. The thermodynamic stability of nitrogen provides an overall driving force for this decomposition, but its favorable rate undoubtedly reflects weaker than normal C-N bonds.



Radical Initiators

Photolytic Bond Homolysis

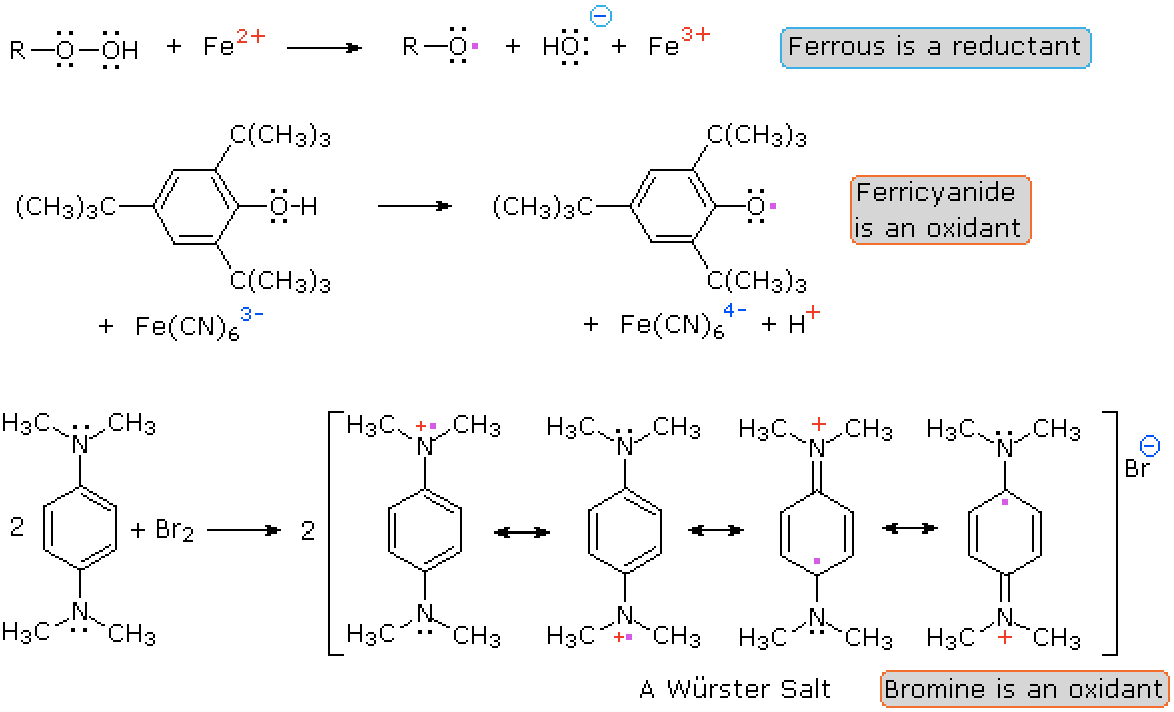
Compounds having absorption bands in the visible or near ultraviolet spectrum may be electronically excited to such a degree that weak covalent bonds undergo homolysis. Examples include the halogens Cl_2, Br_2 & I_2 (bond dissociation energies are 58, 46 & 36 kcal/mole respectively), alkyl hypochlorites, nitrite esters and ketones. Equations illustrating these radical producing reactions are displayed below. The covalent bonds that undergo homolysis are colored red, and the unpaired electrons in the resulting radicals are colored pink. Ketones undergo *n to* π^* *electronic excitation* near 300 nm. The resulting excited state is a diradical in which one of the odd electrons is localized on the oxygen atom. Cleavage of an alkyl group may then take place.



Radical Producing Reactions

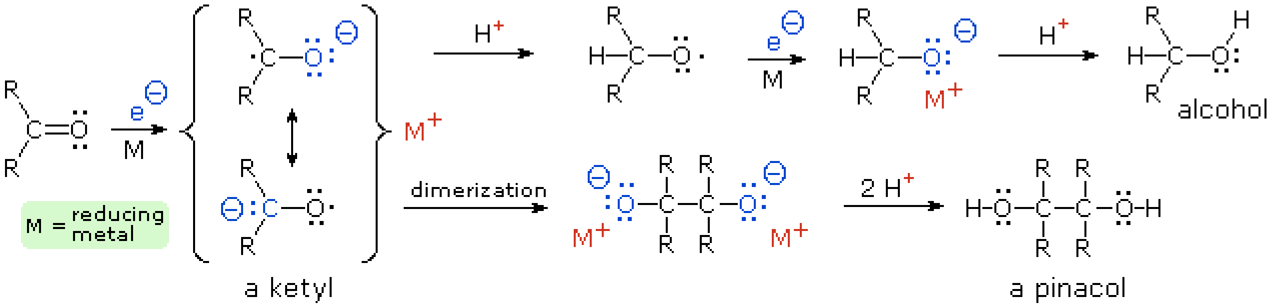
Electron Transfer (It is redox reaction for generation of free radicals)

The action of inorganic oxidizing and reducing agents on organic compounds may involve electron transfers that produce radical or radical ionic species. Ferrous ion, for example, catalyzes the decomposition of hydrogen peroxide (Fenton's reagent) and organic peroxides. In some cases the radical intermediates formed in this manner are sufficiently stable to be studied in the absence of oxygen. The phenoxy radical formed in the second equation below is one such species, Würster's salt (third equation) is another.



Action of Oxidizing and Reducing Agents on Organic Compounds

The alkali metals lithium, sodium and potassium reduce the carbonyl group of ketones to a deep blue radical anion called a "ketyl", shown in the following illustration. Subsequent chemical reactions of these useful intermediates are *discussed elsewhere*. A similar reduction of benzene and its derivatives also proceeds by way of *radical anion intermediates*.



Reduction of Benzene and Derivatives (**It is redox reaction for generation of free radicals)**

Hydrogen and Halogen Atom Abstraction

If free radical reactions are to be useful to organic chemists, methods for transferring the reactivity of the simple radicals generated by the previously described homolysis reactions to specific sites in substrate molecules must be devised. The most direct way of doing this is by an atom abstraction, as shown here.

$$R{-}H + X\bullet \longrightarrow R\bullet + H{-}X$$

Atom Abstraction (**It is redox reaction for generation of free radicals)**

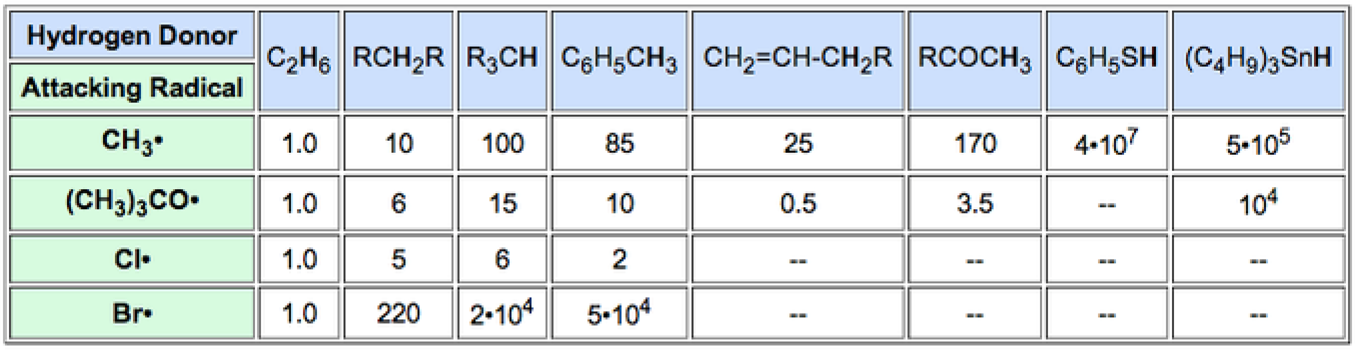
Indeed, when X is Cl or Br, this is a key step in the *alkane halogenation* chain reaction. Hydrogen abstraction reactions of this kind are sensitive to the nature of both the attacking radical (X•) and the R–H bond. This is illustrated by the relative rates of hydrogen abstraction given in the following table. Each horizontal row of data is normalized to 1º C–H (1.0), but there are also large differences between rows. Thus the rate of reaction of 1º C–H with Cl• is a thousand times faster than with Br•. However, the less reactive bromine atom shows much greater selectivity in discriminating between 1º, 2º and 3º C–H groups.

Certain C–H bonds are so susceptible to radical attack that they react with atmospheric oxygen (a diradical) to form peroxides. Typical groups that exhibit this trait are 3º-alkyl, 2º & 3º-benzyl and alkoxy groups in ethers.

$$R{-}H + O_2 \longrightarrow R\bullet + \bullet O_2H \longrightarrow R{-}O{-}O{-}H$$

Hydrogen Abstraction Reaction (**It is redox reaction for generation of free radicals)**

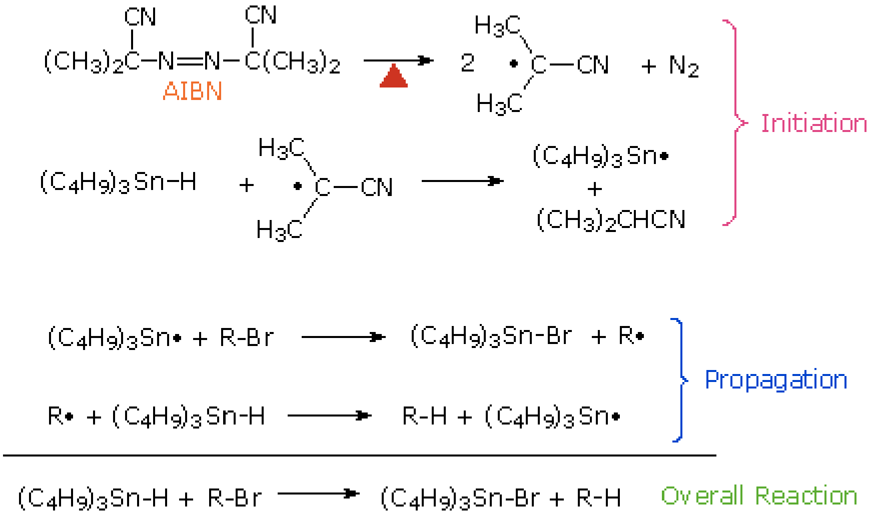
The exceptional facility with which S–H and Sn–H react with alkyl radicals makes thiophenol and trialkyltin hydrides excellent radical quenching agents, when present in excess. At equimolar or lower concentration they function well as radical transfer agents..



Hydrogen Donor Attacking Radical	C_2H_6	RCH_2R	R_3CH	$C_6H_5CH_3$	$CH_2{=}CH\text{-}CH_2R$	$RCOCH_3$	C_6H_5SH	$(C_4H_9)_3SnH$
$CH_3\bullet$	1.0	10	100	85	25	170	$4\bullet10^7$	$5\bullet10^5$
$(CH_3)_3CO\bullet$	1.0	6	15	10	0.5	3.5	--	10^4
$Cl\bullet$	1.0	5	6	2	--	--	--	--
$Br\bullet$	1.0	220	$2\bullet10^4$	$5\bullet10^4$	--	--	--	--

Relative Reactivities (per hydrogen) of Hydrogen Atom Donors with Selected Radicals

Carbon halogen bonds, especially C–Br and C–I, are weaker than C–H bonds and react with alkyl and stannyl radicals to generate new alkyl radicals. This reaction has been put to practical use in a mild procedure for reducing alkyl halides to alkanes. The chain reaction sequence that accomplishes this reduction is shown here. Three examples of this dehalogenation reaction will be displayed.



Reducing Alkyl Halides to Alkanes

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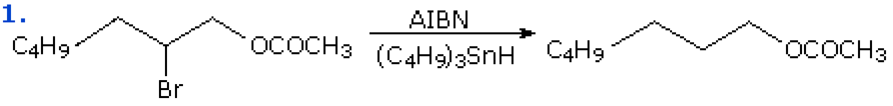

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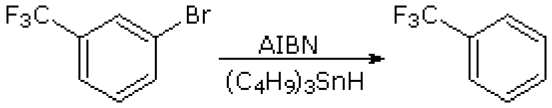

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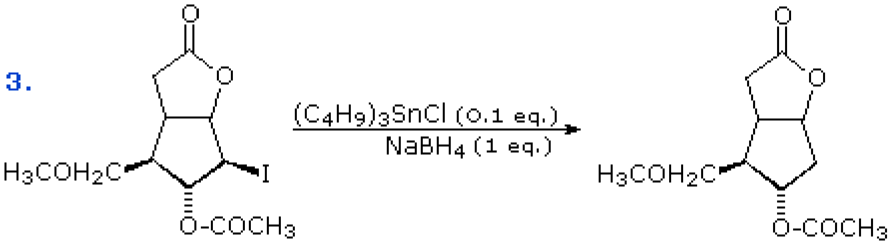

Dehalogenation Reactions

An important modification of this reduction is shown in the third example above. The use of equimolar amounts of tributyltin hydride in reactions presents certain problems, including the toxicity presented by organostannanes, difficulty in separating nonpolar stannanes, such as halides, bis(tributyltin) and bis(tributyltin) oxide from desired products, and formation of tin oxides by reaction with moisture. To reduce these difficulties, a catalytic amount of the stannanes may be used together with enough $NaBH_4$ (or an equivalent reagent) to convert the tributyltin halides to the hydride. Indeed, the reduction is so facile that traces of peroxides in the reactants often initiate reaction without added AIBN.