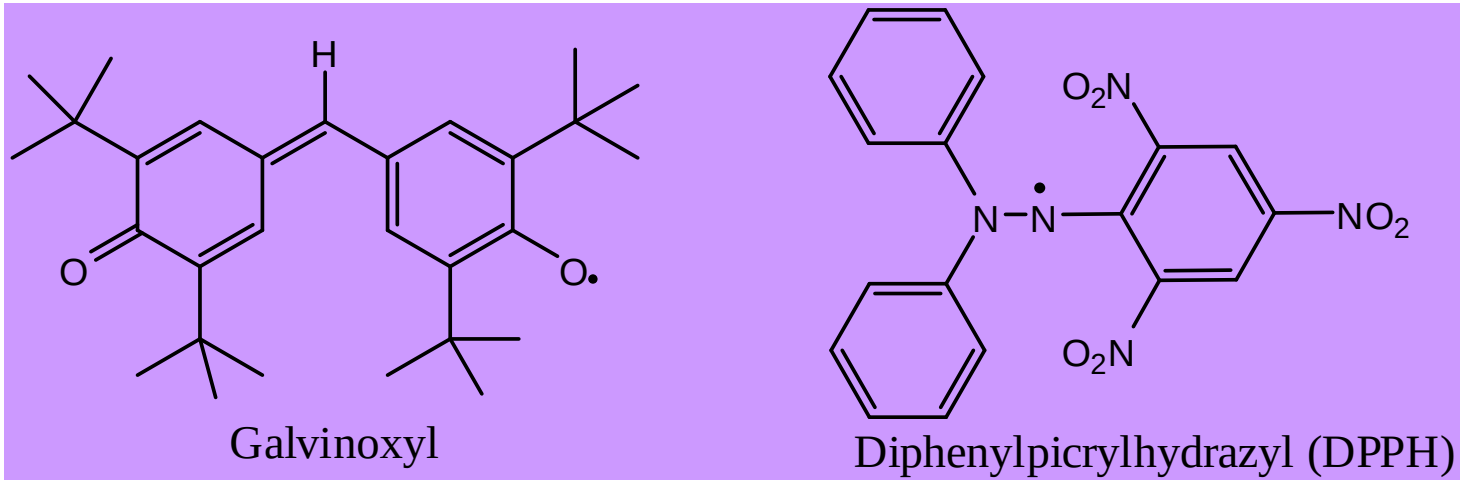
Free Radical

- Stability (thermodynamic) --- Bond Dissociation Energy (BDE)

  $R\text{-}H \rightarrow R\cdot + H\cdot \qquad \Delta H^{o} = BDE$

- Persistency (kinetic) --- steric effects and other stablizing effects

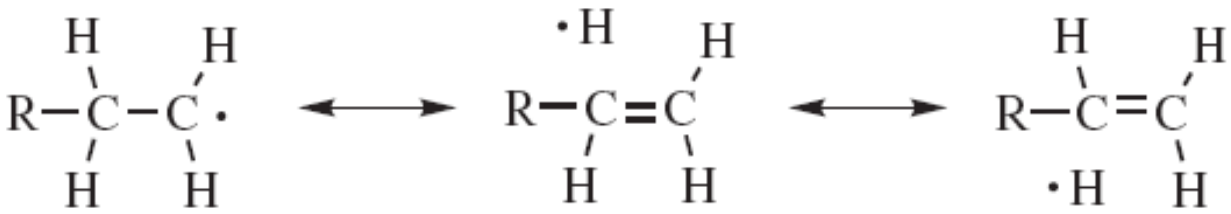


Scheme 2.1 Commercially available free radicals

Stability of free radicals

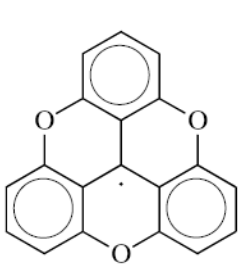
- Hyperconjugation:

tertiary > secondary >primary

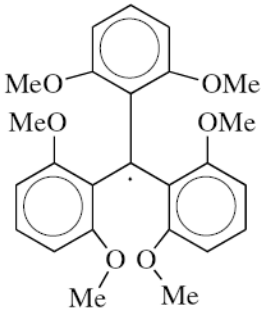


Stability of free radicals

- Hyperconjugation
- Conjugation increases the stability of free radicals.



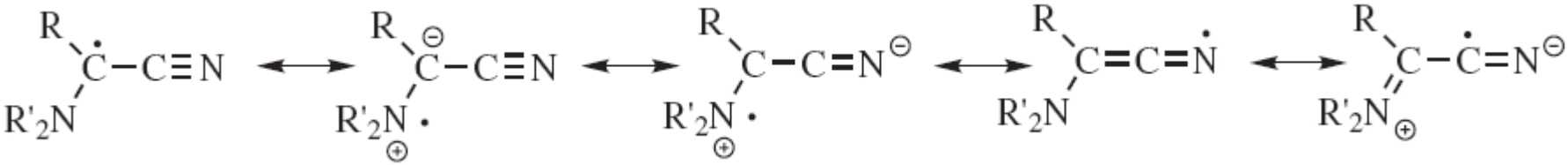
A



B

Stability of free radicals

- Hyperconjugation
- Conjugation increases the stability of free radicals.
- captodative effect (push–pull effect)

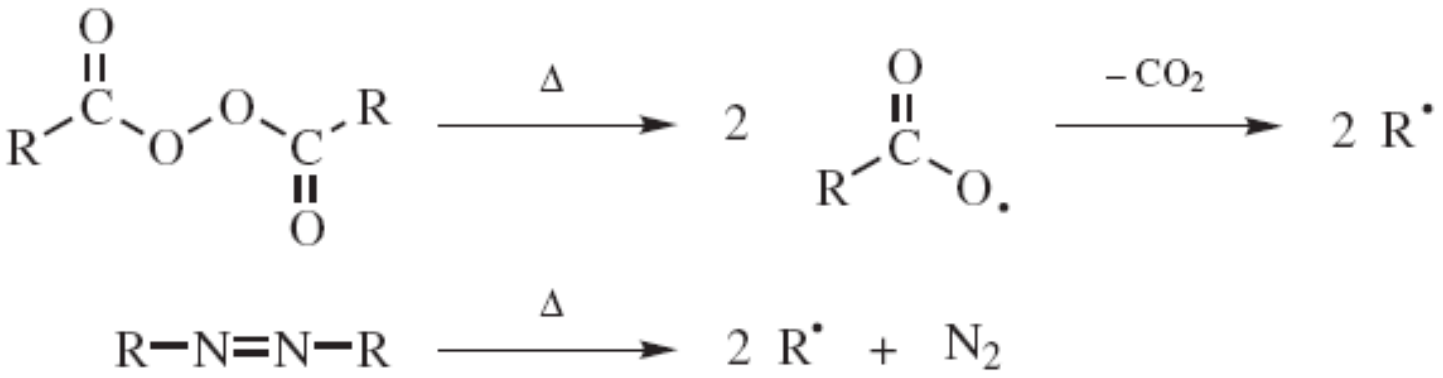


Characterization of radicals

- mass spectrometry (Sablier, M.; Fujii, T. ***Chem. Rev.*** 2002, 102, 2855)
- characterization of alkoxycarbonyl radicals by Step-Scan Time-Resolved Infrared Spectroscopy (Bucher, G.; Halupka, M.; Kolano, C.; Schade, O.; Sander, W. ***Eur. J. Org. Chem.*** 2001, 545.)
- electron spin resonance (esr) or electron paramagnetic resonance (epr)
- Chemically induced dynamic nuclear polarization (CIDNP) (Closs, G.L.; Miller, R.J.; Redwine, O.D. ***Acc. Chem. Res.*** 1985, 18, 196)

Generation of free radicals

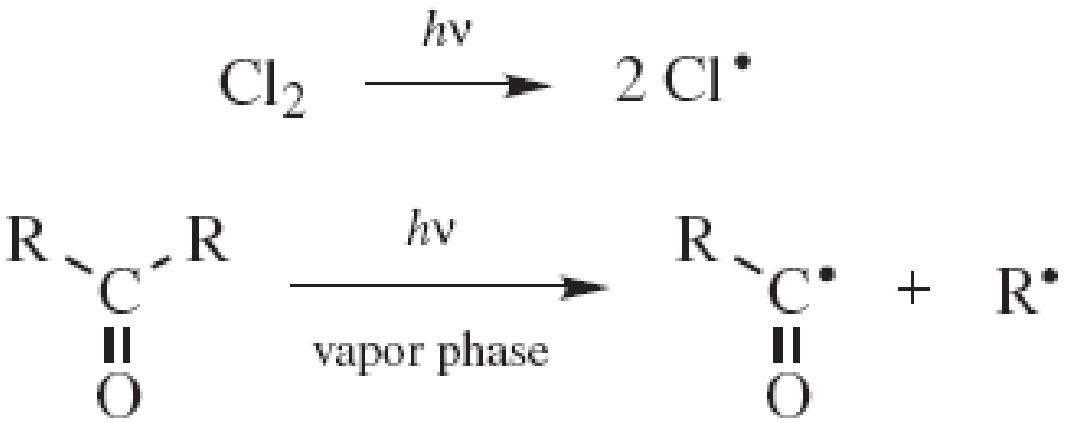
1. Thermal Cleavage.



Generation of free radicals

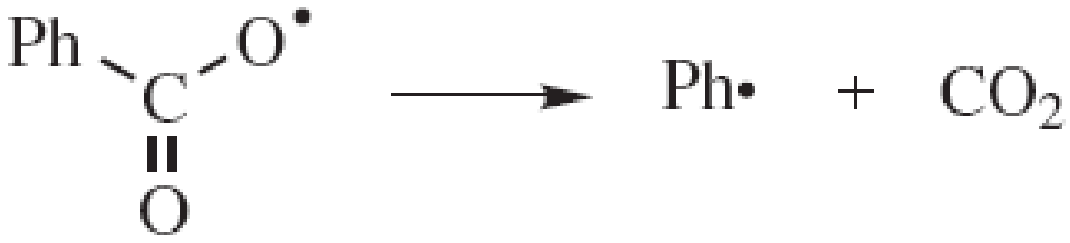
1. Thermal Cleavage.

2. Photochemical Cleavage.



Generation of free radicals

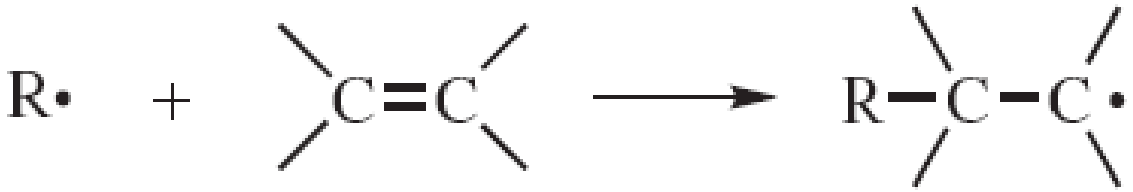
1. Thermal Cleavage.
2. Photochemical Cleavage.
3. Formed from other radicals.
4. Formed by oxidation or reduction, including electrolytic methods.



Radical propagation reactions

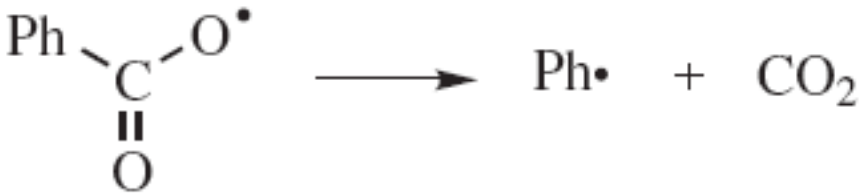
1. Abstraction of another atom or group, usually a hydrogen atom

2. Addition to a multiple bond

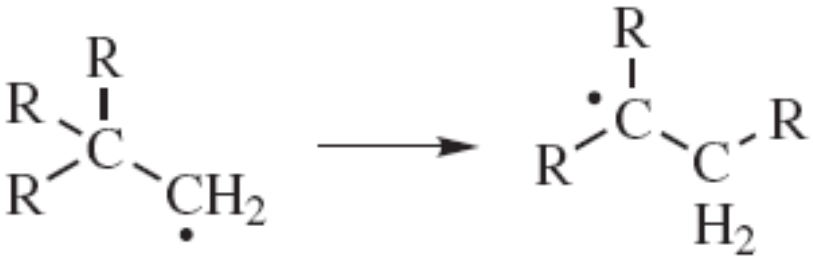


Radical propagation reactions

1. Abstraction of another atom or group, usually a hydrogen atom
2. Addition to a multiple bond
3. Decomposition



4. Rearrangement



The cyclopropylcarbinyradical has found an important application as a radical clock. **(**Griller, D.; Ingold, K.U. ***Acc. Chem. Res.*** 1980, 13, 317**)**

Radical Ions