

VARIOUS RADICAL INITIATION PROCESSES IN ORGANIC SYNTHESIS

Abstract

Radical reactions are one of the most basic kinds of organic transformations that take place via the intermediary of odd electron species. These procedures are crucial for numerous biological and material applications as well as for mechanistic and synthetic organic chemistry. Understanding the fundamentals of both free radical initiation reactions and elementary radical reactions is necessary for the effective use of free radical transformations in organic synthesis. This chapter offers an introduction to the design and initiation of free radical reactions for application in organic synthesis, using illustrative examples from recent literature as a framework. A few reactions are covered, however the main emphasis is on the most significant and adaptable techniques for conducting radical initiation reactions.

Keywords: Radical initiation, Organic chemistry, Techniques

Author

Sayantani Mondal
Department of Chemistry
Bankura Zilla Saradamani Mahila
Mahavidyapith,
Nutanchati, Bankura, West Bengal, India
sayantaniitkgp2006@gmail.com

Radicals are often generated under relatively mild conditions to ensure optimal utility in synthetic transformations. Several routes are available. For example, by homolysis, Radical Initiators (RIs) can produce radicals via breaking relatively weak covalent bonds. These type of homolytic cleavages can easily be achieved by heating the molecule, light absorption (by the molecules containing a chromophore suitable for light absorption), sonolysis (by sound wave), radiolysis (using X-ray, γ irradiation) and the application of mechanical forces (mechanochemistry).

An interesting approach involves leveraging stable radicals such as the reaction of organoboranes with molecular oxygen. This process is convenient for generating carbon-centered radicals at low temperatures.^{1,2,3,4} Alternatively, radicals can be formed by redox reactions. The most straightforward approach involves oxidation of anions or reduction of cations. However, this approach requires pre-generation of such reactive charged species in a separate step. In practice, it is more convenient to transfer an electron to (or from) a closed-shell molecule, leading to the formation of radical cation (or a radical anion). These newly generated radical cations or radical anions then finally collapse to give an anion or cation together with a radical intermediate.

There are numerous literary sources that cover radical initiation.^{5,6,7,8} The usage of thermolysis, photochemical activation, organoboranes, and redox reactions will all be illustrated with a number of examples below.

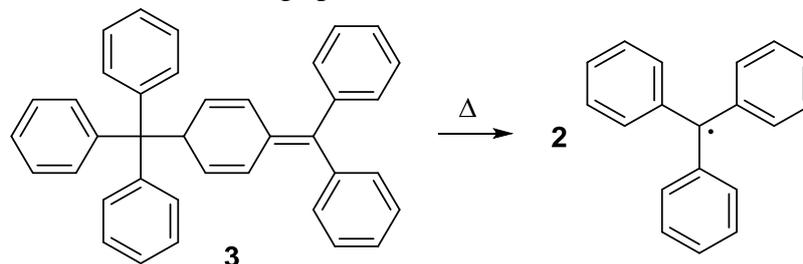
I. THERMOLYSIS

Table 1: Bond dissociation energies of various single bonds (kcal/mol) in organic molecules.⁹

| $\text{CH}_3\text{-X} \longrightarrow \dot{\text{C}}\text{H}_3 + \text{X}\cdot$ | |
|---|----------------|
| X | BDE (kcal/mol) |
| H | 104.9 |
| CH ₃ | 90.1 |
| F | 115 |
| Cl | 83.7 |
| Br | 72.1 |
| I | 57.6 |
| OH | 92.1 |
| OCH ₃ | 83.2 |

In thermolysis, a single bond is homolytically broken to produce a radical species using heat. The RI must have a bond dissociation energy below 40 kcal mol⁻¹ in order to function at a temperature below 150 °C. Thermal initiator design is severely constrained by this necessity. Table 1's representative data on the bond dissociation energy (BDE) of single bonds shows that covalent bonds, which are frequently found in organic compounds, are typically too strong for thermolysis. When the generating radicals are highly stabilized, as in

the case of diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene) methane **3** ($k_d \sim 3 \times 10^{-3} \text{ s}^{-1}$ at 273 K), the cleavage process is accelerated.¹⁰

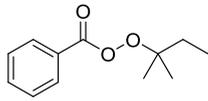
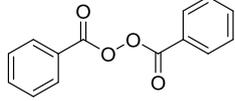
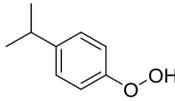
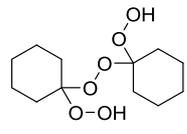
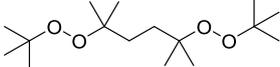
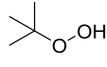
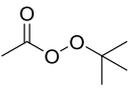
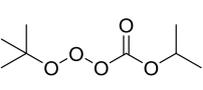
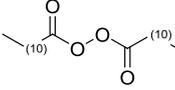
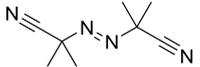
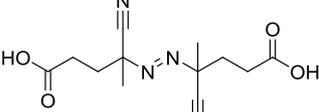


Scheme 1: Thermal cleavage of Diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene)methane.

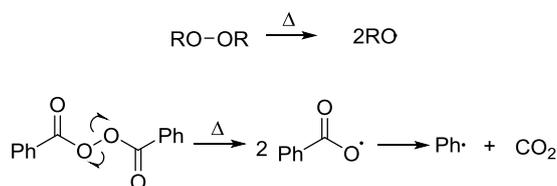
In peroxides, azo compounds, nitrite esters, halogen molecules, N-hydroxy-pyridine-2 thione esters, etc., functional groups that are based on heteroatom-heteroatom or carbon-heteroatom bonds typically better meet the energy requirement for thermolytic radical production. Radical initiators such as organic peroxides and azo compounds leverage formation of a small stable unit for the formation of reactive species (radicals). They are inherently unstable, usually stored at colder temperatures and must be handled with care. For RIs, an appropriate compromise must be found: they must be stable at normal temperature but should disintegrate at a temperature that makes the target radicals easily accessible.

Table 2 provides examples of common organic reactive initiators and their properties.

Table 2: Some common thermal initiators Decomposition rates and 10-hour half-life temperatures.¹¹

| | | | |
|---------------------|---|--|---|
| RI |  |  |  |
| | tert-Amyl peroxybenzoate | Benzoyl peroxide | Cumene hydroperoxide |
| 10h half-life °C | 99 (benzene) | 70 (benzene) | 135 (toluene) |
| K(s ⁻¹) | 4.6x10 | 2.0x10 | 4.0x10 ⁻⁷ , 6.6x10 |
| RI |  |  |  |
| | Cyclohexanone peroxide | 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane | tert-Butyl hydroperoxide |
| 10h half-life °C | 90 (benzene) | 120 (benzene) | 170 (benzene) |
| K(s ⁻¹) | | 1.1x10 ⁻⁵ , 4.7x10 ⁻⁴ | 3x10 ⁻⁷ , 6.6x10 ⁻⁶ , 2.0x10 ⁻⁵ , 3.1x10 ⁻⁵ |
| RI |  |  |  |
| | tert-Butyl peracetate | tert-Butylperoxy isopropyl carbonate | Lauroyl peroxide |
| 10h half-life °C | 100 (benzene) | 98 (aliphatic hydrocarbons) | 65 (benzene) |
| K(s ⁻¹) | 1.2x10 ⁻⁶ , 1.5x10 ⁻⁵ , 5.7x10 ⁻⁴ | | 4.9x10 ⁻⁷ , 9.2x10 ⁻⁶ , 3.8x10 ⁻⁴ |
| RI |  |  | |
| | 2,2'-Azobisisobutyronitrile | 4,4-Azobis(4-cyanovaleric acid) | |
| 10h half-life °C | 65 (toluene) | 69 (water) | |
| K(s ⁻¹) | 2.2x10 | 1.9x10, 9.0x10 | |

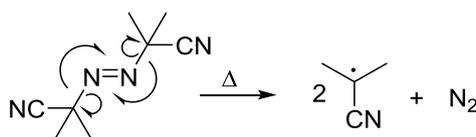
Radicals are frequently produced through the thermolysis of peroxides. With a BDE of 35–50 kcal mol⁻¹, the RO–OR bond is relatively weak and easily breaks to create alkoxy radicals (RO). These kinds of chemical compounds are widely accessible in commerce. Decarboxylation often occurs after the creation of acyloxy radicals in diacylperoxides (**Scheme 2**). Compared to the majority of dialkylperoxides, these peroxides show reduced (O–O) BDE. The lower BDE originates from the resonance stabilization of unpaired electron over the two oxygen atoms in the acyloxy radicals.



Scheme 2: Top: Decomposition of peroxide.

Bottom: Decomposition and fragmentation of benzoylperoxide.

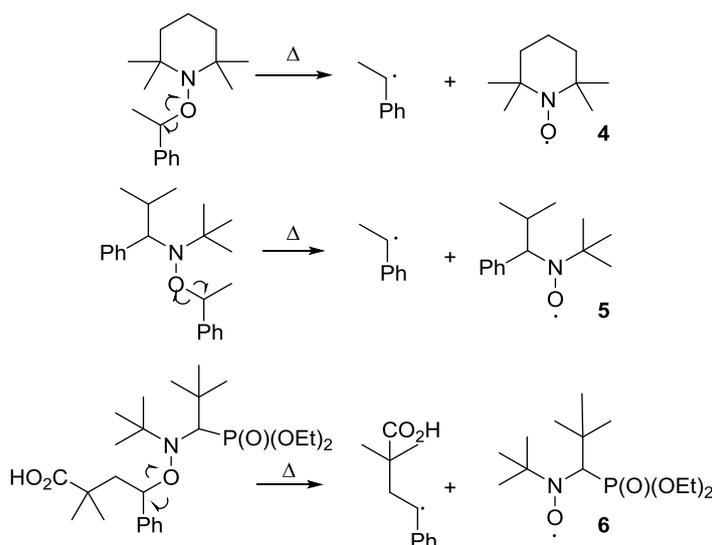
As thermal radical initiators, azo compounds (R-N=N-R) are frequently employed. When N₂ is released thermally (or photochemically, see infra) by these RIs, carbon-centered radicals (R[•]) are formed. The driving force for this process is the creation of N₂, a gas that is extremely stable. The most popular azo chemical for producing radicals in moderate circumstances is 2,2'-azobisisobutyronitrile (AIBN) (**Scheme3**).



Scheme 3: Mechanism of 2,2'-azobisisobutyronitrile decomposition.

Carbon-metal bonds, for example SnR₄ or HgR₂ (R=alkyl, e.g. tetrabutyltin), can also be homolytically cleaved to generate stable radicals. Typically, these reactions take place in the gas phase at very high temperatures (in excess of 180° C).^{12,13} Therefore these organometallic compounds are not generally used in synthetic radical chemistry.

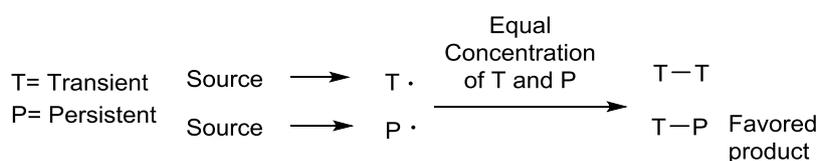
By breaking the O-C link during the thermolysis of alkoxyamines, which has a BDE around 20 to 35 kcal mol⁻¹, nitroxide radicals can be produced. 2, 2, 6, 6-tetramethylpiperidine-N-oxyl (TEMPO, **4**), 2, 2, 5-tri-methyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO, **5**), and N-(2-methylpropyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-N-oxyl (SG1, **6**) are some examples of common nitroxide generating substances. The structures of the alkyl and nitroxide fragments have a significant impact on the rate constants of C-O bond homolysis in alkoxyamines, which typically range from 10⁻³ to 10⁻⁷ s⁻¹ at 350 K (**Scheme4**).^{14,15}



Scheme 4: Decomposition of alkoxyamines to nitroxide radicals **4**, **5**, **6** via thermolysis

Nitroxides, often referred to as “persistent radicals” due to their superstability, are widely applied in organic synthesis and polymer science. In particular, nitroxides are used in

the nitroxide-mediated polymerization (NMP).^{16,17} The persistent radical effect (PRE)¹⁸ is what enables the NMP reaction. The PRE is a phenomenon that occurs in some radical systems and favours the creation of one product to the point where other radical couplings are all but eliminated since one of the radical species is especially stable. As the reaction proceeds, persistent radicals gather in higher amounts. As a result, the reaction proceeds more quickly to produce the desired product (**Scheme 6**)—either by itself in a termination step or by combining with the persistent radical. This polymerization process is referred to as "living" since it does not naturally self-terminate. This is because the chains continue to develop under favourable reaction circumstances whenever there is a reactive monomer to "feed" them. Due to the PRE, it is possible to suppose that at any given time, almost all of the growing chains are "capped" by a mediating nitroxide, meaning that they dissociate and grow at remarkably similar rates, resulting in a generally uniform chain length and structure.¹⁹



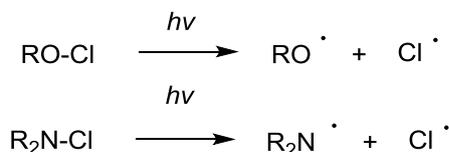
Scheme 5: General mechanism of Nitroxide-mediated Polymerization (NMP)

II. PHOTOCHEMICAL ACTIVATION

Also allowing for homolytic breakage of bonds is ultraviolet or visible light. In comparison to the ground state S_0 , the bond cleavage in excited states (singlet or triplet) is more favourable. The weakening of bonds in excited states is caused by the promotion of an electron, frequently from the highest occupied molecular orbital (HOMO) (corresponding to a bonding or nonbonding orbital) to the lowest unoccupied molecular orbital (LUMO), corresponding to an antibonding orbital. Due to its ability to be initiated selectively and under relatively benign circumstances, photoinduced homolysis can be useful. Additionally, stronger bonds (such C-C bonds) can be broken, and side reactions are typically less common.²⁰

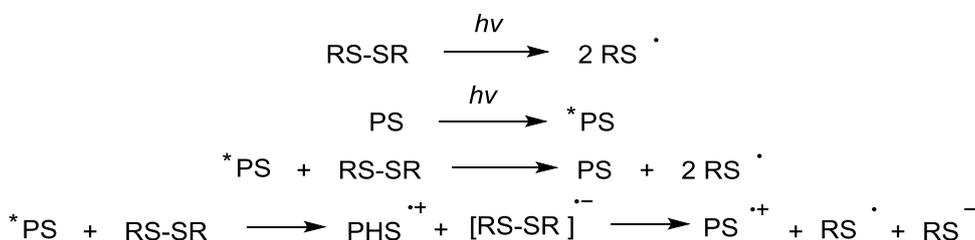
The photolysis of peroxides²¹ or acylperoxides²² forming alkoxy or acyloxy radicals is well established. The majority of these precursors are light-absorbing at wavelengths around <300 nm. Special glassware must be used because every day glassware absorbs light at <310 nm. The same thing needs to be taken into account for azo compounds, as they exhibit a very mild absorption at wavelengths greater than 300 nm. An obvious exception to this general pattern may be found in AIBN, which has an absorption band that is relatively intense about 340 nm.

It has also been documented that photolysis of derivatives of organohalides that possess relatively weak C-halogen bonds occurs. Due to their substantial absorption at $200 < \lambda < 350$ nm, iodides and bromides are utilised more frequently, with iodides being able to cleave more effectively.^{23,24} Hypochlorites (RO-Cl) and N-chloroamines (R₂N-Cl) are two examples of heteroatom-heteroatom linkages that are photolyzed together with the matching alkoxy and aminyl radicals, **Scheme 6**.²⁵



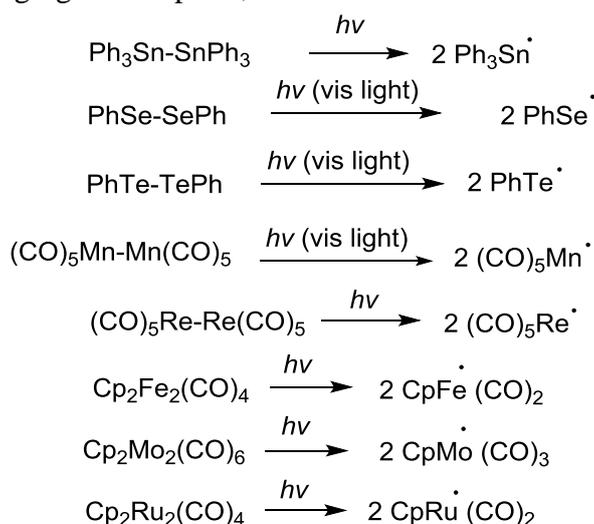
Scheme 6: Photolysis of weak heteroatom-heteroatom bonds

The S-S bond in disulfides can also be photolyzed to produce thiyl radicals, however this process has low light absorption of the precursor at $\lambda > 320$ nm, as shown in **Scheme 7**. A photosensitizer (PS) with tailored light absorption qualities can promote bond homolysis by energy transfer and/or electron transfer.²⁶ Many physical chemistry investigations on thiyl radicals have employed this method with success.^{27,28} Under more favourable circumstances, restrained disulfides, such as lipoic acid, which has a well-defined absorption band at about 350 nm, can be cleaved.²⁹



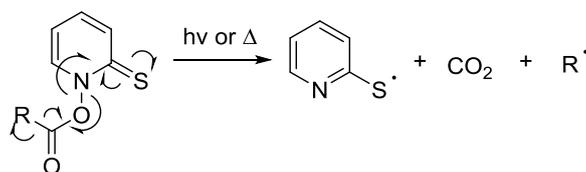
Scheme 7: Photochemical generation of Thiyl radicals

Tin radicals are produced by photolysis of alkyliditin compounds, and they are crucial in the field of synthetic radical chemistry.³⁰ Various compounds with a Se, Te, Mn, Re, Fe, Mo, or Ru atom may benefit from additional photoinduced metal-metal bond breaking processes (**Scheme 8**).^{31,32,33,34,35,36,37} This primarily has to do with the $\sigma\text{-}\sigma^*$ transition, which makes sure that following light absorption, a dissociative excited state form.

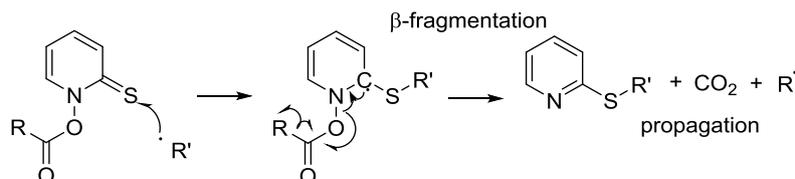


Scheme 8: Photolysis of metal-metal bonds to generate metal centered radicals

In organic synthesis, xanthates have additionally shown themselves to be effective organic radical initiators. Specifically, *N*-hydroxypyridine-2-thione esters (or *N*-hydroxyquinazoline-4-thiones) derivatives^{38,39} and *N*-hydroxypyridine-2-thione carbamates⁴⁰ were proposed as efficient sources of carbon-centered and aminyl radicals, respectively. The latter species can also be accessed by thermolysis.⁴¹ *N*-hydroxypyridine-2-thione esters are highly interesting reagents since they allow initiation of chain reactions (see review⁴²). An addition/-fragmentation sequence is used to carry out the propagation step (**Scheme 8**). A carbon-centered radical is produced by the exothermic insertion of an R[•] radical to the C=S bond. With the simultaneous production of an aromatic ring, a favourable β-fragmentation (which is equivalent to a monomolecular reaction) takes place, and eventually, a new radical is generated following decarboxylation (R[•], **Scheme 10**).

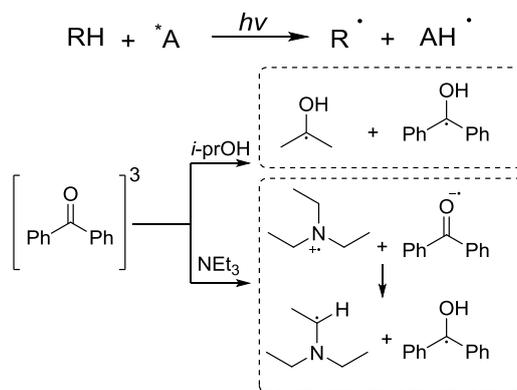


Scheme 9: Radical generation process in *N*-hydroxypyridine-2-thione esters



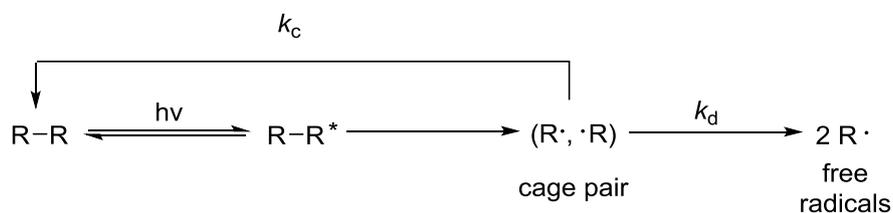
Scheme 1: Addition/ β-fragmentation process occurring in *N*-hydroxypyridine-2-thione esters.

By using photolysis to create radicals, hydrogen abstraction is another useful process. This typically happens in a molecule in its triplet state T_1 (which is the case for most molecules possessing a carbonyl group).⁴³ The absorption characteristics can be modified from the UV (benzophenone) to the near visible (thioxanthone) or the visible wavelengths (camphorquinones, coumarins, dyes, etc.) using a wide variety of precursors. According to **Scheme 11**, this reaction either involves the transfer of hydrogen or involves an electron transfer followed by a proton transfer (e-/H⁺ mechanism).



Scheme 2: Sequence of hydrogen transfer and electron-proton transfer for the triplet state of benzophenone.

An important phenomenon known as the cage effect, which occurs predominantly in thermolysis and photochemical reactions where a radical pair is formed, was first recognized by Frank and Rabinowitch in the 1930s.^{44,45} The solvent molecules have the ability to create a “cage” around a formed radical pair (RP). The radicals coexist for a certain amount of time as seen in **Scheme 3** **Error! Reference source not found.** Radicals can easily recombine in such an RP, where the two radicals have opposite spins, before escaping from the solvent cage, where this recombination takes place. The rate of recombination between the two radicals is typically extremely high. The temperature and solvent viscosity have a significant impact on cage effect. The recombination in the geminate RPs should be as minimal as possible for an effective radical initiation. This ratio of inside to outside the cage is typically not negligible. Only 60% of the radicals that escape the cage and are prepared to start a chain reaction during the thermolysis of AIBN have been observed to have an average value of roughly 20%.⁴⁶



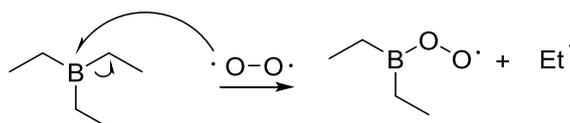
Scheme 3: In the solvent cage, radical pairs can recombine to varying degrees, depending on the solvent.

A radical cage pair is produced when a generic dimer in solution is photolyzed. The radicals in the solvent cage have two options: they can combine again to form the parent dimer or they can diffuse apart to produce free radicals. For radical-radical recombination and radical diffusion out of the cage, respectively, the rate constants are k_c and k_d .⁴⁷

III. ORGANOBORANE ACTIVATION

Trialkyl boranes are useful in the generation of alkyl radicals because they can be generated simply by an interaction with molecular oxygen (

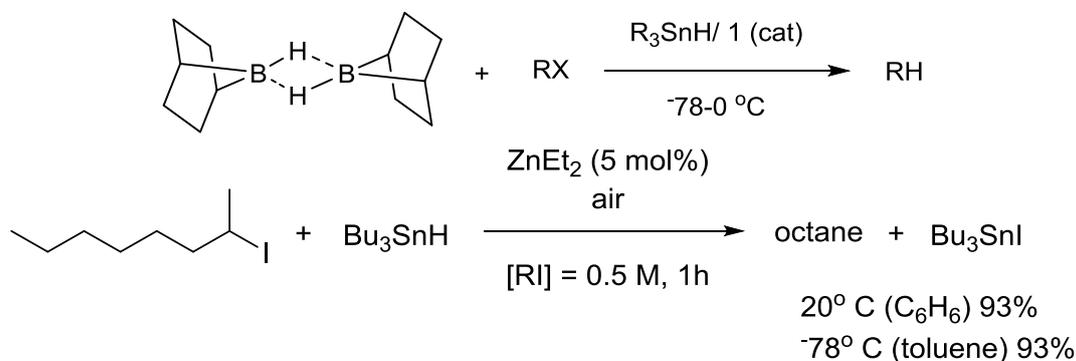
Scheme 4). This oxidation can be quite efficient.^{48,49,50}



Scheme 4: Ethyl radical production for the triethylborane/O₂ system

The most common reagent used is triethylborane, which has been utilized in various organic transformations. Et₃B can function as an effective radical generator even at very low temperatures (at -78 °C), in contrast to other usual initiators that are activated by thermolysis

(such as peroxides or azo compounds). This is very useful when trying to initiate stereospecific reactions. These reactions only require traces of oxygen to form the alkyl radicals. Et_2Zn and 9-borabicyclo (3.3.1) nonane (9-BBN) have also been shown to be capable of starting radical reactions when exposed to oxygen.^{51,52}



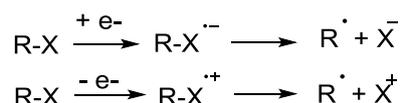
Scheme 5: 9-borabicyclo[3.3.1] nonane as an initiator for low-temperature free-radical

Bottom: Initiation of tin-mediated radical reactions by diethylzinc-air.reductions.

Sulfonyl radicals have found considerable use in synthetic organic chemistry, specifically for their ability to add to double and triple bonds.^{53,54} A new method for the generation of sulfonyl radicals from aryl and alkyl sulfonylbromides involves autooxidation of triethylborane at ambient temperature. The resulting sulfonyl radical could be trapped via addition to terminal alkynes yielding (*E*)-bromo vinylsulfones selectively.⁵⁵

IV. REDOX REACTIONS

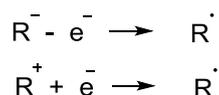
Redox reactions with the right precursor (R-X), can also produce radicals. Because it produces just one radical rather than two, the redox process has an inherent advantage over thermolysis and photolysis.



Scheme 6: Only one radical species is generated using redox processes.

The precursor (R-X) interacts with highly oxidising substances such metal salts of cerium (IV), manganese (III), and silver (II) through the oxidation route.^{56,57} These substances have the ability to oxidise a wide range of other substances while also producing free radicals as a byproduct. The precursor (R-X) must take an electron from an appropriate donor for the reduction process. Radiation is frequently produced by adding an electron to halides. The halogen atom's electronegativity ensures that the matching radical anion $\text{RX}^{\cdot-}$ will produce X^- as a result. For the reductive production of R, complexes of samarium, iron, copper, and ruthenium are utilised. Additionally, organic single electron transfer reductants have been produced.^{58,59}

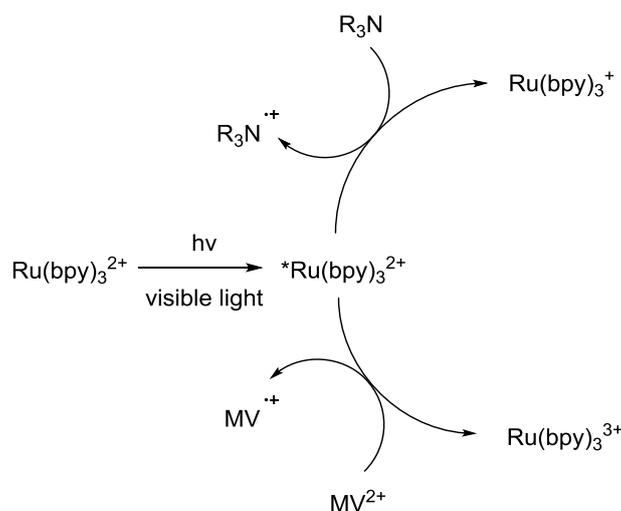
Radical production can also result from the direct electrochemical oxidation (or reduction) of a cation or an anion (**Scheme 16**).^{60,61,62}



Scheme 7: Radicals from direct oxidation (reduction) of anions (cations)

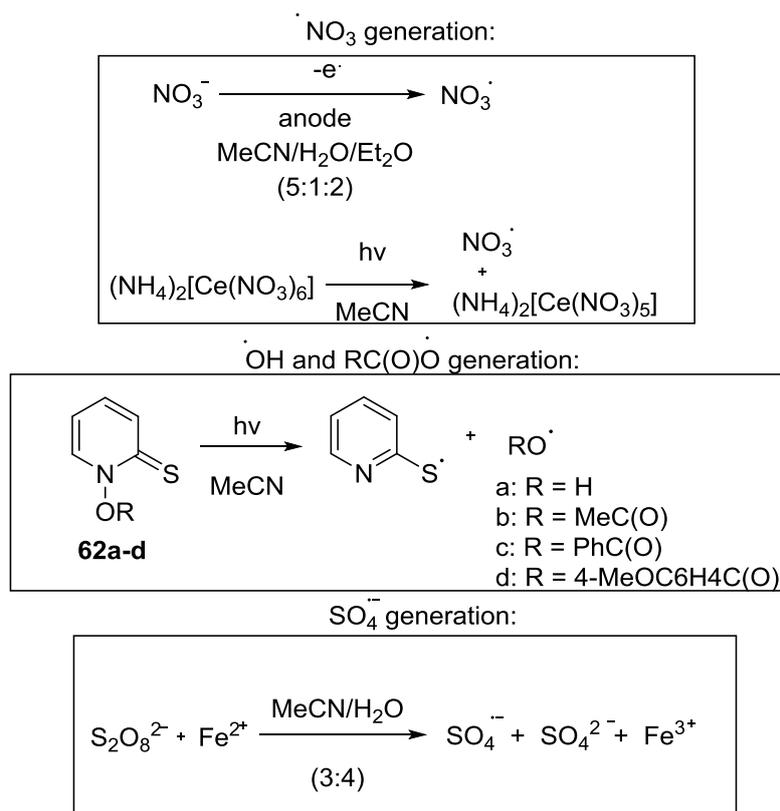
Light can also accelerate redox reactions because excited states are more effective oxidising or reducing agents than comparable ground states. Additionally, there has been a lot of interest in photochemically induced electron transfer from transition metals, especially for synthetic applications.^{63,64,65,66,67} In *photoredoxorganocatalysis*, this procedure is crucial. The chosen photocatalysts $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ir}(\text{ppy})_2(\text{dtb-bpy})]^+$ are primarily based on Ru or Ir and exhibit strong visible light absorption. Conveniently, these substances can be employed with visible light sources, such as fluorescent lights and natural sunshine.

According to the mechanism, a strongly reducing or oxidising metal complex is produced when the excited state of the organocatalyst reacts with a sacrificial quencher via an electron transfer reaction (amine, methyl viologen, enamine, etc.). For instance, the excited state of $^*\text{Ru}(\text{bpy})_3$ is reduced (or oxidised) by an amine (or methyl viologen (MV^{2+})) to produce $\text{Ru}(\text{bpy})_3^+$ (or $\text{Ru}(\text{bpy})_3^{3+}$) (**Scheme 17**). A strong $\text{Ir}(\text{ppy})_2(\text{dtb-bpy})$ reductant for $\text{Ir}(\text{ppy})_2(\text{dtb-bpy})^+$ is produced when the matching excited state reacts with a sacrifice enamine.



Scheme 8: $\text{Ru}(\text{bpy})_3^+$ and $\text{Ru}(\text{bpy})_3^{3+}$ formation via a light-activated mechanism.

Anodic oxidation of inorganic nitrates or photoinduced electron transfer from Ce^{IV} nitrates, such as ceric ammonium nitrate (CAN), can produce interesting inorganic radicals including NO_3^\cdot , $\text{SO}_4^{\cdot-}$, OH^\cdot , NO_2^\cdot .^{68,69} Thiopyridone **62a** was photolyzed to produce $\text{SO}_4^{\cdot-}$ and OH^\cdot , which were then produced using the Fe^{II} /peroxo disulfate redox system (**Scheme 18**).⁷⁰



Scheme 9: Preparative scale generation of NO₃[·], SO₄^{·-}, OH[·] and RC(O)O[·] in solution. For a more detailed account of radical initiators see “Overview of Radical Initiation.”⁷¹

V. CONCLUSION

In the synthetic world, the free radical has gone from being viewed as unmanageable and unpredictable to being accepted as necessary chemistry. It is aiming towards mild and neutral radical initiation conditions, compatibility with a wide variety of functional groups, a reduced propensity for rearrangements and *b*-eliminations, a wide range of order-of-magnitude reaction rates, and a remarkable degree of chemoselectivity. Thus, free radical initiations and conversions are now an essential part of the synthetic toolkit and are no longer optional. The difficulties posed by traditional methods of radical creation have been overcome by modern approaches. Catalysis of radical initiation is now more practical as a result of this understanding. It is admirable that this distinctive chemistry is slowly making its way into the industrial sector through flow photoreactors. The initiation, propagation and termination nature of radical chemistry continues to fascinate both theoreticians and experimentalists.

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