XX

Radical Kinetics and Clocks

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1   INTRODUCTION

The interest in organic radical chemistry increased tremendously in recent decades as synthetic methods for using radicals in fine chemical synthesis were refined and the occurrence of radical intermediates in productive biological processes became better understood. Both for synthetic planning with radicals and for mechanistic understanding of processes involving radical transients, the rate constants of radical reactions are critically important. Most radicals are highly reactive transients that couple with one another with diffusion-controlled rates, but most productive radical reactions require that the radicals react with closed-shell molecules with velocities that minimize the extent of radical–radical reactions. In order to achieve that condition in a preparative reaction, one must control velocities by the concentrations of reagents, and synthetic planning is greatly simplified when the rate constants for the radical reactions are available. The concept of applying radical kinetics for synthetic planning is well accepted by all contemporary organic chemists, and many radical rate constants were determined by organic chemists for that specific objective.

Radical rate constants can be measured directly in physical chemistry laboratories equipped with fast detection methods, typically by UV–visible spectroscopy, and pulse irradiation methods such as laser flash photolysis (LFP) or pulse radiolysis for generation of radicals. Alternatively, indirect kinetic methods can be accomplished in most organic chemistry preparative laboratories. In an indirect method, products from competitive reactions are quantified after work-up by a spectroscopic or chromatographic technique, and the ratio of products, concentrations of reagents, and the known rate constant for one of the competing reactions, the so-called basis reaction, is used to determine the rate constant for the reaction of interest. This simple approach requires no special instrumentation, and it has been widely applied, often by chemists who wish to use the information in designing new conversions, and most of the radical kinetic data used in synthetic planning has come from indirect studies.

Radical reaction rate constants are an integral part of the description of radical reactions, and they are contained in most of the sections of this encyclopedia for the specific radicals of interest in each article. A comprehensive listing of radical kinetics is beyond the scope of this article, but absolute rate constants are listed here for representative values for some common reactions to demonstrate trends. The major focus of this article is on the application of competition kinetic studies that can be applied for a wide range of radical reactions and a cataloging of various types of "radical clocks" that can be used in competition studies.

When a radical process used as a basis reaction in indirect studies is a first-order rearrangement, the reaction is commonly termed a *radical clock*, an appellation used by Griller and Ingold in a seminal review published in 1980.[1] That report established guidelines for competition kinetic studies and can be credited with generally informing the organic community of the availability and utility of the methods. Radical clocks provide an obvious advantage

in experimental design because the basis reaction is self-contained, and one does not need to control concentrations of a trapping reagent. Nonetheless, the range of kinetics for which any given radical clock can be applied is limited because one cannot alter the rate constant of the clock reaction. Therefore, a collection of radical clocks with a wide range of rate constants is desired for studies of new reactions with various reactivities. In practice, such a repertoire of radical clocks exists for alkyl radicals,[2] but clocks for carbon-centered radicals with stabilizing groups and for heteroatom-centered radicals are less well established. In this article, radical kinetics and indirect kinetic methods are described with an emphasis on radical clocks. Direct kinetic studies are discussed in **Analysis of Radicals by EPR** and **Structures and Reactivity of Radicals Followed by Magnetic Resonance**, Volume 1.

2   CHAIN AND NONCHAIN RADICAL REACTIONS

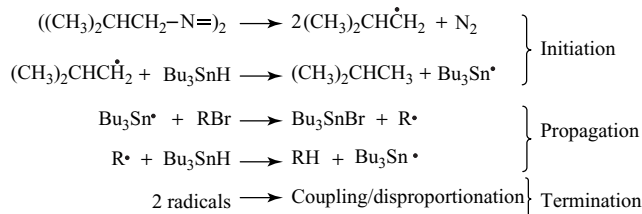### 2.1   Examples of Chain and Nonchain Radical Reactions

Productive radical methods can involve either chain reactions or nonchain reactions, which are described briefly here for reference in the kinetic discussions that follow. Most chemists are familiar with chain reaction applications, which are the most common. Nonchain radical reactions are less familiar, but they can be very useful for fine chemical synthesis and highly controlled radical polymerizations.

A radical chain reaction sequence is composed of three parts, initiation, propagation, and termination, as exemplified in the tin hydride reaction of an alkyl bromide shown in Figure 1. Radicals are formed in the initiation reactions, typically by thermolysis or photolysis of an initiator (see **Overview of Radical Initiation**, Volume 1). The initiation sequence can be a single reaction that gives radicals that enter into a subsequent propagation reaction or a sequence of reactions as shown in Figure 1. The productive steps in the chain sequence are the propagation reactions. In each individual propagation reaction, the product radical is a reactant radical for another propagation step. The propagation sequence can be simple, involving only one or two elementary reactions, or it can be complex with many competing reactions. The termination reactions involve radical–radical reactions, either couplings or disproportionations, that give closed-shell products. In principle, a variety of radical–radical termination reactions could be occurring in a chain sequence, but that is seldom the case. Because many chain termination reactions occur at diffusion control, the major termination pathway will be radical–radical reactions between the most abundant radical at steady state, which is controlled by the relative rate constants of the elementary propagation steps. For example, in the chain sequence in Figure 1, the $Bu_3Sn^•$ radical reacts with RBr with a second-order rate constant that is about 100 times larger than that for the reaction of radical $R^•$ with Bu_3SnH. An absolute condition of the chain sequence is that the two propagation reactions have the same velocity, and, in the case where the concentrations of alkyl halide and tin hydride are equal, this requires that the $R^•$ concentration at steady state is 100 times as great as the $Bu_3Sn^•$ concentration. Therefore, if all radical–radical reactions occur at diffusion control, then 99% of the termination events will involve reactions of two $R^•$ radicals.

Nonchain radical reactions also can be applied productively for synthesis. The hallmark of a nonchain sequence is that one of the radical intermediates is persistent under the reaction conditions, a condition that arises because self-termination of that radical is slow or reversible. For example,
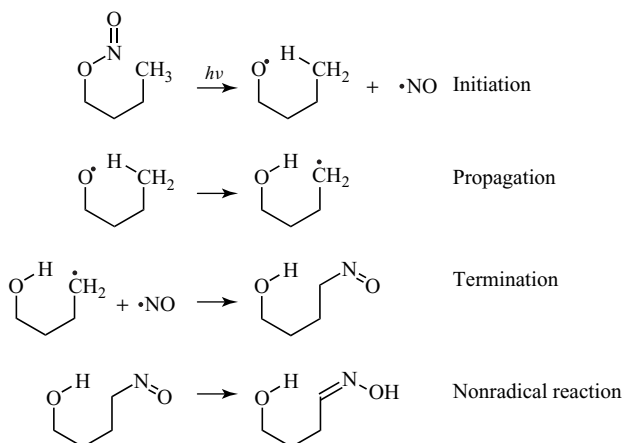
$$((CH_3)_2CHCH_2-N{=})_2 \longrightarrow 2(CH_3)_2CH\overset{•}{C}H_2 + N_2$$
$$(CH_3)_2CH\overset{•}{C}H_2 + Bu_3SnH \longrightarrow (CH_3)_2CHCH_3 + Bu_3Sn^•$$
Initiation

$$Bu_3Sn^• + RBr \longrightarrow Bu_3SnBr + R^•$$
$$R^• + Bu_3SnH \longrightarrow RH + Bu_3Sn^•$$
Propagation

$$2\ radicals \longrightarrow Coupling/disproportionation$$
Termination

Figure 1   Tin hydride reduction of an alkyl bromide. Elementary steps in the radical chain reduction of an alkyl bromide with tin hydride.

Figure 2 The Barton reaction. Photolysis of the nitrite ester gives an alkoxyl radical and the NO radical, which is persistent. Internal hydrogen atom transfer of the alkoxyl radical gives the carbon-centered radical that is trapped by NO to give the nitroso compound. Rearrangement of the nitroso compound to an oxime is a nonradical reaction.

nitroxyl radicals lacking β-hydrogen atoms such as the 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) radical have small equilibrium constants for dimerization, and the ·NO radical is stable with respect to coupling. The persistent radical is reactive with other radicals, however, and when it accumulates to a relatively high concentration, it captures all other radicals in cross-termination reactions because of its high concentration. The general phenomenon where all radicals cross-couple without multiple propagation steps is termed the *persistent radical effect* or the *Ingold–Fischer effect* for the authors who initially described it succinctly (see **Nitroxides in Synthetic Radical Chemistry**, Volume 2 and **Fundamentals of Controlled/Living Radical Polymerization**, Volume 4).[3,4]

The Barton reaction,[5] illustrated in Figure 2, is a nonchain radical reaction that involves the ·NO radical. In this reaction, photolysis of a nitrite ester gives the ·NO radical and an alkoxyl radical, which can recombine in a nonproductive step. The alkoxyl radical can abstract a hydrogen atom from a neighboring carbon atom to give an alkyl radical, and the alkyl radical formed in this process will react with the ·NO radical in a termination reaction to give a nitroso compound that rearranges to an oxime in a nonradical process.

2.2 Kinetics of Radical Chain Reactions

Chain reactions have a unique set of rate expressions, and an understanding of radical chain reaction kinetics can be useful in the design of efficient conversions. The key points in a chain reaction are that (i) each propagation step in the chain sequence must have the same velocity and that (ii) under steady-state conditions that are obtained in a chain sequence, the velocity of the initiation sequence is equal to the velocity of the termination sequence. Because of these equalities, a series of steady-state assumptions can be made that result in the rate law for the chain reaction in terms of a few key rate constants for elementary reactions. Importantly, the rate constant for the slow step in the chain reaction, termed the *rate-controlling step*, is the only elementary propagation rate constant that appears in the rate law. For the radical chain reduction of an alkyl bromide with tin hydride shown in Figure 1, an alkyl radical reacts with tin hydride with a rate constant of about $2 \times 10^6 \, \text{M}^{-1} \, \text{s}^{-1}$ at room temperature,[6] and the $\text{Bu}_3\text{Sn}^\bullet$ radical reacts with an alkyl bromide with a rate constant that is about 100 times greater.[7] If the reaction is initiated by thermal decomposition to azo-*bis*-isobutyrylnitrile (AIBN), then the total rate law for the chain reaction is given in (1). In (1), k_{init} is the first-order rate constant for the initiator homolysis step,[8] f is the fraction of initiator radicals that escape from the solvent cage, k_{SnH} is the second-order rate constant for the rate-controlling reaction of alkyl radical with tin hydride, and k_{term} is the second-order rate constant for termination, often equal to 25% of the diffusion control rate constant due to the spin statistical requirement that radicals have proper

spin orientations to form singlet products, which occurs in 25% of the encounters of two odd-electron species.[9] The rate law will be similar for photochemical initiation, but the k_{init} and f terms are replaced by the photon flux and quantum yield of the photolysis and, if the solution is not opaque, the absorbance.

$$\frac{d[\text{RX}]}{dt} = \frac{k_{\text{init}} f [\text{AIBN}]^{1/2} k_{\text{SnH}} [\text{Bu}_3\text{SnH}]}{2 k_{\text{term}}^{1/2}} \quad (1)$$

With general knowledge of the rate constants for the elementary processes, one can predict the velocity of chain reaction. Consider the reduction of RBr with Bu_3SnH using AIBN initiation in refluxing benzene with the following concentrations: $[\text{RBr}]_0 = [\text{Bu}_3\text{SnH}]_0 = 0.2\,\text{M}$; $[\text{AIBN}]_0 = 0.005\,\text{M}$. The rate constants at $80\,^\circ\text{C}$ are $k_{\text{init}} = 2 \times 10^{-4}\,\text{s}^{-1}$ for AIBN homolysis, $k_{\text{SnH}} = 6.4 \times 10^6\ \text{M}^{-1}\,\text{s}^{-1}$, $k_{\text{term}} = 1 \times 10^{10}\,\text{s}^{-1}$, and $f \approx 0.5$. Under these conditions, the velocity of the chain reaction is about $3 \times 10^{-4}\,\text{M}\ \text{s}^{-1}$, and the reaction would be complete in about 15 minutes. Substituting the slower reacting $(\text{Me}_3\text{Si})_3\text{SiH}$ ($k_{\text{SiH}} = 1.3 \times 10^6\,\text{M}^{-1}\,\text{s}^{-1}$ at $80\,^\circ\text{C}$) for the tin hydride would increase the reaction time to about 1 hour.

The importance of the rate-controlling reaction is readily understood by example. If one replaced RBr with RI as a radical precursor in the tin hydride example, the rate of reaction of $\text{Bu}_3\text{Sn}^{\bullet}$ with RI would be increased to the diffusion-control limit, but the reaction of $\text{R}^{\bullet}$ with Bu_3SnH would be unchanged. Therefore, the transient concentration of $\text{Bu}_3\text{Sn}^{\bullet}$ would be reduced, but the overall velocity of the process would not be affected provided that the initiation reaction was unchanged. Alternatively, replacing the tin hydride with tris(trimethylsilyl)silane would result in a reduced rate for the overall reaction as noted above. In addition, the overall reaction also would be slowed if RBr was replaced with RCl as the radical precursor. In this case, the rate constant for the reaction of $\text{Bu}_3\text{Sn}^{\bullet}$ with RCl is appreciably smaller than that for the reaction of the stannyl radical with RBr and, in fact, even smaller than that for the reaction of $\text{R}^{\bullet}$ with tin hydride.[7] The rate law for the overall reaction (1) would now contain the rate constant for the reaction of the stannyl radical with the alkyl chloride, and the velocity of the reaction would be reduced if other experimental details were unchanged.

2.3   Radical Chain Initiation Kinetics

In many conversions, radical chain reactions are initiated thermally by decomposition of an added initiator. For reactions conducted at elevated temperatures, Walling reported the following temperatures that gave 1-hour half-lives for decomposition of commercial or synthesized radical initiators (see **Overview of Radical Initiation**, Volume 1)[8]: di-*tert*-butyl peroxyoxalate, $45\,^\circ\text{C}$; di-*tert*-butyl hyponitrite, $55\,^\circ\text{C}$; AIBN, $81\,^\circ\text{C}$; benzoyl peroxide, $91\,^\circ\text{C}$; *tert*-butyl peroxybenzoate, $125\,^\circ\text{C}$; and di-*tert*-butyl peroxide, $150\,^\circ\text{C}$. As a general rule, these temperatures can be considered to be typical reaction temperatures for the use of the particular initiator or a closely related initiator. A variety of thermal initiators exist, but it is noteworthy that Barton's PTOC (pyridine-2-thioneoxycarbonyl) ester radical precursors (see below for an example) decompose thermally in refluxing solvents such as tetrahydrofuran (THF) or toluene.[10] Barton's PTOC esters also decompose when irradiated with visible light, which provides a convenient method for radical chain initiation at reduced temperatures.

A relatively new method of thermal initiation involves addition of a small amount of Et_3B to a reaction mixture that has not been degassed thoroughly.[11] The borane reacts with oxygen, apparently to generate ethyl radicals. The kinetics of this reaction are not available, but the reaction is known to be efficient at low temperatures, and this is an attractive method for initiation of radical reactions when one wishes to maintain low reaction temperatures to achieve selectivity in the conversions.

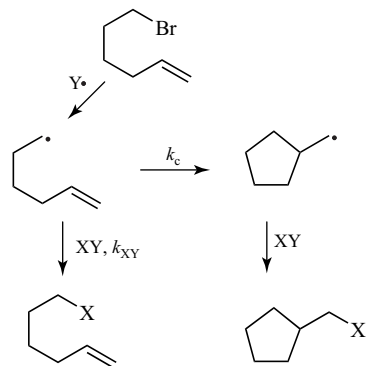## 3   COMPETITION KINETICS AND RADICAL CLOCKS

3.1   Overview of Competition Kinetics

Although sophisticated instrumentation is needed for measuring radical kinetics due to the short lifetimes and small concentrations of radicals in typical reactions, kinetic studies can be accomplished in most wet chemistry laboratories without any special instrumentation by the use of competition experiments. The concept of the study is that a reaction with a known rate constant competes with

Figure 3 Reactions in a competition kinetic study. The 5-hexenyl radical cyclization competes with trapping by reagent XY, and the rate constant for the trapping reaction can be determined from the ratio of acyclic to cyclic products, the concentration of XY, and the known rate constant for cyclization.

the reaction with the unknown rate constant, and the unknown rate constant can be calculated from the product ratio obtained after the reaction, the concentrations of reagents employed, and the known rate constant. An example of a competition kinetic study is shown in Figure 3. In this sequence, the radical precursor, 6-bromo-1-hexene, reacts with $Y^{\bullet}$ to give the 5-hexenyl radical, which is a "radical clock." The clock cyclizes to the cyclopentylmethyl radical with a known rate constant (k_c), and the rate constant of interest is that for the reaction of trapping agent XY with the primary radical (k_{XY}). Because the cyclization reaction in this example is effectively irreversible, the rate constant for trapping the cyclic radical is not important. The ratio

of products is determined after the reaction, and the rate constant k_{XY} is calculated from that ratio, the concentration of trapping agent XY, and the known cyclization rate constant k_c.

3.2 Kinetic Expressions in Competition Kinetics

In a competition kinetic study, the products formed in the competing reaction are quantified, and the rate constant for the reaction of interest is determined from this product ratio, the concentrations of reagents, and a known rate constant for the basis reaction. If a unimolecular radical reaction (i.e., a radical clock, see below) is employed, the reaction is a first-order process by definition. From a practical perspective, it is most convenient to use large excesses of reagents in bimolecular processes such that pseudo-first-order conditions are maintained. Nonetheless, true second-order kinetics with changing concentrations of reagents can be handled with the correct kinetic expression. Table 1 contains the kinetic expressions that apply to some of the more common experimental designs.

The precision necessary for a rate constant is a function of the desired application. When high precision is needed, one should study the reaction with a variety of concentrations of the radical trapping agent to prevent errors due to reversibility of the clock reaction. Many first-order radical reactions are effectively irreversible, but the following example

Table 1 Kinetic expressions for competition kinetic experiments.[a]

Type of study	Kinetic expression
First-order (k_1) vs pseudo-first-order (k_2)	$k_1/k_2 = ([R^1X]/[R^2X])([XY]_m)$
First-order (k_1) vs second-order (k_2)	$k_1/k_2(\ln([XY]_i + k_1/k_2) - \ln([XY]_f + k_1/k_2)) = [Sub]_I ([R^2X]/[R^1X]) (1 + ([R^2X]/[R^1X]))^{-1}$
Pseudo-first-order (k_1) vs pseudo-first-order (k_2)	$k_1/k_2 = ([RX^1]/[RX^2]) ([X^2Y]_m/[X^1Y]_m)$
Second-order (k_1) vs second-order (k_2)	$k_1/k_2 = (\ln([X^1Y]_i/([X^1Y]_i - [RX^1])))/ (\ln([X^2Y]_i/([X^2Y]_i - [RX^2])))$
Reversible first-order(k_1) vs pseudo-first-order (k_2)	$(k_1/k_2)(k_{2'}/(k_{-1} + k_{2'}[XY]_m)) = [R^1X]/[R^2X]$

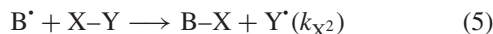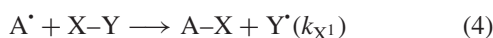[a] In these expressions, the trapping agent is XY, which reacts by transfer of X to the radical. The subscript in $[XY]_i$ indicates initial concentration, that in $[XY]_f$ indicates final concentration, and that in $[XY]_m$ indicates average concentration. The rate constants k_x in the kinetic expressions are shown in the type of study column in parentheses. Products with superscripts 1 and 2 are those formed in the first and second reaction, respectively, in the type of study column.
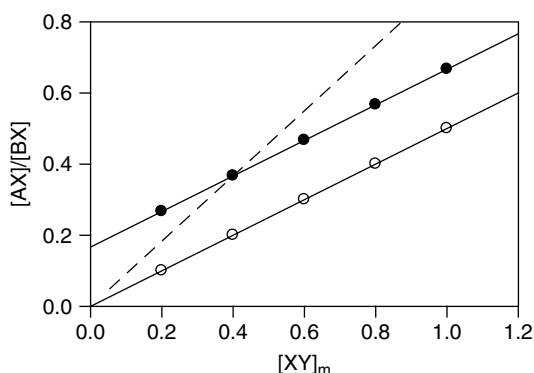
illustrates the potential problem of reversibility. Ring opening of the cyclopropylcarbinyl radical (see Section 4) is a well-recognized fast radical reaction, and this reaction has been used as a competition reaction in many indirect kinetic studies. The equilibrium constant for the cyclopropylcarbinyl radical at $20\,^{\circ}C$ strongly favors the ring-opened product ($K \approx 10\,000$ at room temperature).[12] In the phenyl-substituted analog, the cyclopropylbenzyl radical, the ring opening of the cyclopropyl group is reasonably fast ($k = 6 \times 10^4$ s^{-1} at $20\,^{\circ}$C[12]), but the ring-opened product is disfavored ($K = 0.012$ at room temperature).[12,13] Nonetheless, the benzylic radical can still be used as a competing reaction in a competition study with appropriate caution.

A determination of a second-order rate constant at a single concentration of reagent would not provide a unique rate constant unless the trapping reaction of the ring-opened radical was fast relative to the back-reaction. However, this problem is avoided if one conducts a series of reactions at a variety of concentrations. Figure 4 illustrates the situation for the case where radical A$^{\bullet}$ equilibrates with B$^{\bullet}$, and both radicals react with trapping agent XY to give products AX and BX. In this case, the ratio of products will change with the concentration of the trapping agent as shown in the idealized plot in Figure 4. The rate constants in this situation are described by (6). Note that the rate constants for the back-reaction and trapping reaction of the rearranged radical are not needed to obtain the rate constant for the trapping reaction of radical A$^{\bullet}$ with XY.

$$A^{\bullet} \longrightarrow B^{\bullet}(k_{R1}) \qquad (2)$$

$$B^{\bullet} \longrightarrow A^{\bullet}(k_{R2}) \qquad (3)$$

$$A^{\bullet} + X\text{–}Y \longrightarrow A\text{–}X + Y^{\bullet}(k_{X1}) \qquad (4)$$

$$B^{\bullet} + X\text{–}Y \longrightarrow B\text{–}X + Y^{\bullet}(k_{X2}) \qquad (5)$$

$$\frac{AX}{BX} = \frac{k_{X1}k_{R2}}{k_{X2}k_{R1}} + \frac{k_{X1}}{k_{R1}}[X\text{–}Y]_m \qquad (6)$$

3.3   Basis Reactions for Radical Clocks

Any kinetic method could be used to calibrate a radical clock, and several clocks were calibrated by direct EPR or UV–visible spectroscopy with flash lamp or LFP methods to generate the radicals. However, many carbon radical clocks were calibrated indirectly with a limited number of trapping agents. The two most common methods, the tin hydride method and the PTOC–thiol method, can be used for a wide range of radicals and are illustrated in this section.

Figure 4   Results from hypothetical competition kinetics experiments for a radical clock reacting in the presence of bimolecular trapping reagent XY used in excess where the rearrangement has $k_{R1} = 1$ s^{-1}, and the trapping reaction has $k_{X1} = 0.5$ M^{-1} s^{-1}. When the rearrangement is effectively irreversible, $k_{R2} \approx 0$ s^{-1}, then the plot with an intercept at the origin (open symbols) is obtained. If the clock rearrangement is reversible with rate constant $k_{R2} = 3$ s^{-1} and the trapping rate constant for the rearranged radical is $k_{X2} = 1$ M^{-1} s^{-1}, then the plot with the solid symbols is obtained. The slopes of the lines give k_{X1}/k_{R1}, which is the same for both cases. If the reversible clock was studied only at 0.4 M concentration of XY with the assumption that the reaction was not reversible, however, then the dashed line would be obtained, and the derived trapping reaction rate constant would be in error by nearly a factor of 2.

3.3.1   The Tin Hydride Method

In the tin hydride method, the radical precursor is a halogen or pseudo-halogen and tributyltin hydride or another group 14 hydride is used as the trapping agent (see **Tin Hydrides and Functional Group Transformations**, Volume 2). Group 14 metal hydrides are the most completely calibrated family of radical trapping agents, and rate constants for reactions of Bu_3SnH, Ph_3SnH, $(Me_3Si)_3SiH$, and Et_3SiH with many carbon-, nitrogen-, and oxygen-centered radicals are known.[14] The most widely used reagent for calibration has been Bu_3SnH, which reacts with alkyl radicals with

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rate constants that were determined using LFP methods in the early 1980s.[6,15] These directly measured rate constants were combined with previously determined relative rate constants to give absolute rate constants for clock reactions. For example, cyclization of the 5-hexenyl radical in competition with tin hydride trapping was quite well studied by Walling in the late 1960s and early 1970s,[16] and combination of the relative rate constants for those processes with the absolute tin hydride values gave absolute rate constants for cyclization of the 5-hexenyl radical and launched contemporary radical clock chemistry.

The experimental design for a tin hydride competition study is illustrated in Figure 3. The radical precursor typically is an alkyl halide or pseudohalide, although other radical precursors can be used. Tin hydride or other group 14 hydride is used in excess so that pseudo-first-order reaction conditions are maintained. In early studies, reactions were usually initiated by thermolysis of AIBN or a similar initiator at temperatures between 70 and 110 °C. In more recent studies, radical initiation by reaction of triethylborane with oxygen at room temperature or reduced temperatures has been common.

As in synthetic applications of radical chemistry, a competition kinetic study requires an efficient chain reaction sequence. For group 14 hydrides, tin and germanium hydrides react fast enough with alkyl radicals to maintain chain conditions, but trialkylsilanes such as Et_3SiH do not. The substituted $(Me_3Si)_3SiH$ (see **Silanes as Reducing Reagents in Radical Chemistry**, Volume 2) reacts considerably faster with alkyl radicals than common silanes, and this reagent is an excellent hydrogen atom trapping agent for alkyl radicals. For trapping more reactive radicals such as aryl, vinyl, and oxyl radicals, Et_3SiH is adequately reactive to propagate chain reactions.

In regard to the radical precursor limitations, the group 14 trialkylmetal radical must react efficiently with the precursor. Silyl radicals are highly reactive with various halides or pseudohalides, but stannyl radicals react only sluggishly with alkyl chlorides. For aryl and vinyl radical generation, iodides are recommended as the radical precursors. There is no direct counterpart for heteroatom radical generation in the tin hydride protocol.

3.3.2 The PTOC thiol method

The PTOC thiol method is a kinetic adaptation that employs Barton's PTOC esters (anhydrides of a carboxylic acid and the thiohydroxamic acid N-hydroxypyridine-2-thione) as radical precursors (Figure 5). In this method, the PTOC ester reacts to give an acyloxyl radical, and decarboxylation of the acyloxyl radical gives the target radical. The target radical can react with a wide range of
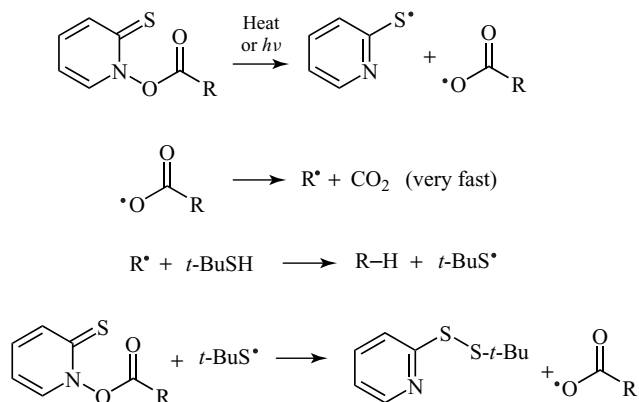
Figure 5 Fundamental reactions in the PTOC thiol method. The radical precursor is a mixed anhydride of a carboxylic acid and the thiohydroxamic acid, N-hydroxypyridine-2-thione, termed a PTOC ester. The PTOC ester decomposes thermally or photochemically with visible light irradiation to give an acyloxyl radical that rapidly decarboxylates to give the radical of interest. Reaction of that radical with a thiol competes with a rearrangement (not shown). The thiyl radical reacts with another PTOC ester molecule to give the disulfide product and another acyloyxl radical.

hydrogen atom donors including the highly reactive thiophenol and benzeneselenol (selenophenol), and the radicals formed from the hydrogen atom transfer step react with another molecule of PTOC ester in a propagation step.

The PTOC thiol method has two significant advantages over the tin hydride method as well as two significant disadvantages. Owing to the high reactivity of the thione group in the PTOC ester and related radical precursors, a wide range of propagating radicals can be used including any group 14 atom centered radical and the group 16 thio- and seleno-centered radicals. This feature opens the kinetic method to the use of highly reactive H-atom transfer agents, such as benzeneselenol. In addition, the PTOC ester methodology has been extended to the production of nitrogen- and oxygen-centered radicals, which were not readily available in the tin hydride method. On the negative side, the high reactivity of the thione group results in relatively efficient reactions of the precursors with carbon-centered radicals,[17] and it is difficult to "time" a slow carbon radical reaction by this method because the radical precursor will intercept the carbon-centered radicals in a "self-trapping" reaction. The other disadvantage of the method is due to the requisite intermediacy of the acyloxyl radicals; acyloxyl radical precursors to aryl and vinyl radicals will not decarboxylate rapidly enough to avoid some trapping of these radicals by many H-atom trapping agents.

4   RADICAL CLOCKS

Competition kinetic methods commonly employ radical clocks,[1] which are calibrated unimolecular radical reactions. The clock reactions are cyclizations, fragmentations including ring openings, or migrations that involve initial cyclizations and subsequent ring openings. The primary advantage of a radical clock is that the competition reaction is self-contained and additional reagents are not necessary, but this property works to limit the useful dynamic range of a clock.

4.1   Carbon Radical Clocks

Alkyl radical clocks are the most numerous, with calibrated clocks ranging in rate constants at room

temperature from $300 \, s^{-1}$ to greater than $3 \times 10^{11} \, s^{-1}$. Table 2 contains a representative selection of alkyl radical clocks.[6,15,16,18–30] This collection is intended to show the breadth of calibrated clocks employing examples that are not especially difficult to prepare and whose products are reasonably easy to characterize. The Arrhenius functions should be considered operational equations that predict rate constants reasonably well but do not necessarily provide highly accurate entropies and enthalpies of activation. Most of the kinetic values were determined from competition kinetic studies using the rate constant for the reaction of Bu_3SnH as the basis reaction, which illustrates the fundamental importance of the tin hydride rate constants.[6,14]

Substituted alkyl radical clocks are well represented in the context of 5-exo cyclizations with rate constants in the range of 1×10^5 to $1 \times 10^8 \, s^{-1}$ at room temperature (Table 3).[6,16,31–35] A noteworthy point of these rate constants is the similarity of the values for both series of monosubstituted (i.e., secondary) radicals. For the tertiary radicals, however, significant reductions in rate constants were observed for the planar conjugated radicals (carboethoxy and cyano substituents), and this effect is most likely due to steric compression in obtaining the transition state for cyclization as opposed to stabilization due to the substituent.[34]

Some benzyl radical clocks are available. A problem with these clocks is that the high stability of the benzyl radical limits the number of reactions possible. For example, the 5-exo cyclization shown in Figure 6 is slow,[21] and the ring opening of the cyclopropylbenzyl radical, while reasonably fast, is reversible with the cyclic product favored.[12,13] For the (2-phenylcyclopropyl)benzyl radical, the phenyl

$k = 3 \times 10^2 \, s^{-1}$

$k = 6.1 \times 10^4 \, s^{-1}$

$k = 5.4 \times 10^6 \, s^{-1}$

$k = 2 \times 10^8 \, s^{-1}$
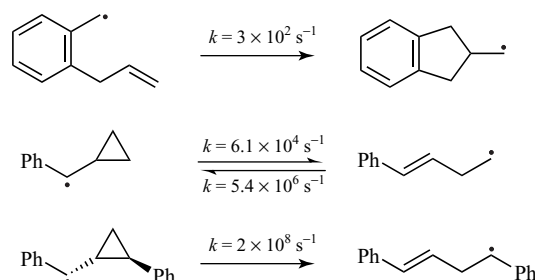
Figure 6   Examples of benzyl radical clocks. The rate constants are for reactions at room temperature.
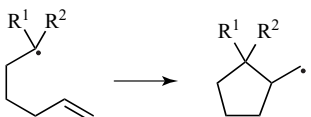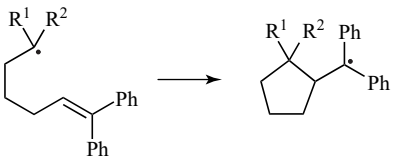
Table 2 Representative alkyl radical clocks.[a]

Reaction	Arrhenius function	$k_{(20°C)}$ $(s^{-1})^b$	Basis[c]	References
	$12.6 - 12.2/\theta$	300	Tin hydride	18–20
	$11.55 - 11.82/\theta$	500	Tin hydride	21
	$13.2 - 13.5/\theta$	1300	Tin hydride	22
	$10.37 - 6.85/\theta$	1.8×10^5	Tin hydride	6, 16
	$11.00 - 5.88/\theta$	4.1×10^6	Tin hydride	6
	$9.9 - 4.4/\theta$	4.1×10^6	Tin hydride	15, 23
	$13.1 - 8.0/\theta$	1.3×10^7	Direct	24
	$10.40 - 3.63/\theta$	4.9×10^7	Direct	25
	$13.15 - 7.05/\theta$	7.8×10^7	Various	26
	$12.7 - 5.04/\theta$	2.5×10^8	Direct	27
	$13.0 - 5.2/\theta$	1.3×10^9	PhSeH	28, 30
	$13.9 - 3.3/\theta$	2.7×10^{11}	PhSeH	29
	$13.1 - 2.0/\theta$	5×10^{11}	PhSeH	29

[a] Arrhenius function in which the activation energy is in kcal mol^{-1}; $\theta = 2.3RT$ in kcal mol^{-1}.
[b] Rate constant at 20 °C.
[c] Basis method for measuring the clock reaction; tin hydride competition, direct studies via laser flash photolysis, or benzeneselenol competition.

groups at the radical center and incipient radical center cancel one another, and the rate constant for ring opening is similar to that for ring opening of the unsubstituted parent, the cyclopropylcarbinyl radical.[36] It is noteworthy that all three of the benzyl radical reactions shown in Figure 6 are about 3 orders of magnitude slower than the reactions of the corresponding primary alkyl radicals.

Table 3   Rate constants for substituted alkyl radical clocks

R^1	R^2	$k_{(20\,°C)}$ (s^{-1})^a	References
H	H	1.8×10^5	6, 16
CH$_3$	H	1.1×10^5	31
CH$_3$	CH$_3$	2.6×10^5	31
CO$_2$Et	H	1.4×10^5	31
C(O)NEt$_2$	H	0.9×10^5	32
OCH$_3$	H	1.6×10^5	31

H	H	3.7×10^7	25, 33
CH$_3$	H	2.2×10^7	33
CH$_3$	CH$_3$	1.1×10^7	33
CO$_2$Et	H	5×10^7	34
C(O)NEt$_2$	H	2×10^7	32
OCH$_3$	H	4×10^7	34
OH	CH$_3$	9.1×10^7	35
CO$_2$Et	CH$_3$	3.3×10^5	34
C(O)NEt$_2$	CH$_3$	3×10^5	32
CN	CH$_3$	2.1×10^5	34

^{a} Rate constants at 20 °C in units of s^{-1}.

Aryl and vinyl radical clocks are not well represented. In early studies, diacylperoxide precursors to the phenyl and 2,2-dimethylvinyl radical were irradiated with laser light with the intention of producing the corresponding acyloxyl radical that could decarboxylate. Rate constants for reactions of tin hydride were determined in these studies,[15] but it was later learned that the initially formed acyloxyl radicals did not decarboxylate completely before reaction with the tin hydride.

In more recent studies, a rate constant for the reaction of an aryl radical with tin hydride at room temperature was determined to be $k = 7.8 \times 10^8\,\text{M}^{-1}\,\text{s}^{-1}$.[37] If this value is used with previous competition kinetic results, the rate constants at 25 °C for cyclization of the aryl radicals shown in Figure 7 are 5×10^8 and 8×10^9 s^{-1} at room temperature.[15] The relative rate constant
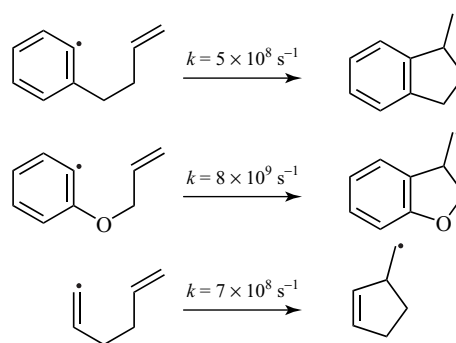
Figure 7   Examples of aryl and vinyl radical clocks. The rate constants are for reactions at room temperature.

for cyclization of vinyl radical in Figure 7 and trapping by tin hydride is 0.9 M at 80 °C.[38] If one assumes that the rate constant for tin hydride
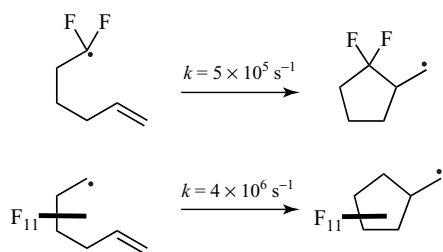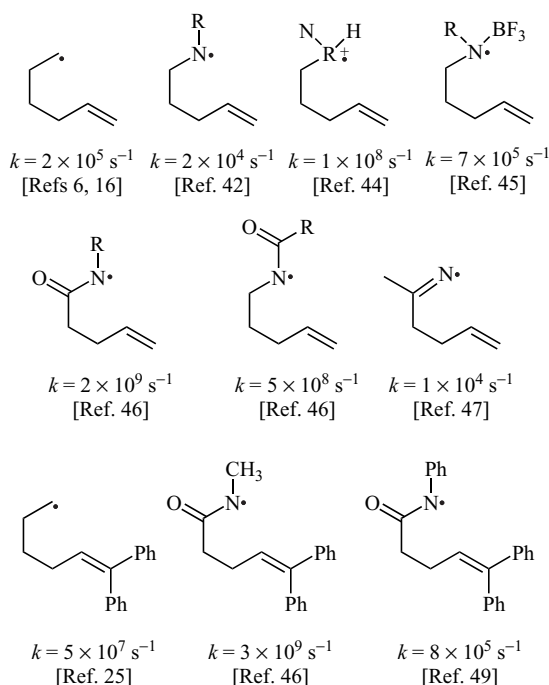
Figure 8 Examples of fluorocarbon radical clocks. The rate constants are for reactions at $30\,^{\circ}$C.

Figure 9 Nitrogen radical clocks that react by cyclizations. The rate constants for 5-exo cyclizations at room temperature are listed.

reaction with the vinyl radical is equal to that for reaction with the aryl radical, then the rate constant for cyclization of the vinyl radical clock in Figure 7 is 7×10^8 s^{-1}; the assumption is based on the fact that vinyl and alkene C–H bond energies are quite similar.

Products from fluorocarbon radical reactions are of high commercial interest owing to the stability of the polymers and the low refractive index of fluorocarbons. Cyclizations of a series of fluorine-containing 5-hexenyl radicals[39] and other fluorine-containing radical cyclizations[40] have been studied. Two examples are shown in Figure 8.[39]

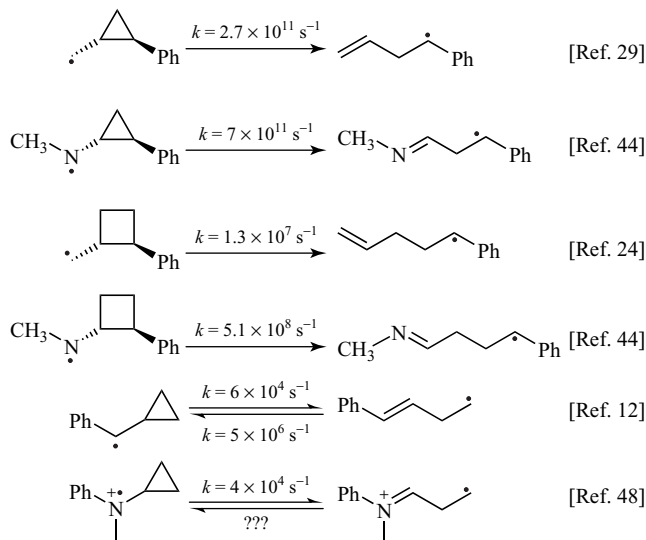## 4.2   Nitrogen Radical Clocks

A number of nitrogen-centered radical clocks have been calibrated, most by direct LFP. Some early nitrogen radical clock calibrations were attempted by the kinetic EPR method,[41] but the method is difficult to interpret when no comparative values are available. The advantage of the direct LFP approach is that absolute kinetic values can be obtained with good accuracy and precision in many cases, but the disadvantage is that the clocks might not be appropriate for a wide range of studies. In order to detect the products in LFP studies, many of the clocks were designed to give UV–visible detectable benzylic or diphenylalkyl radicals. In indirect studies with these clocks, these relatively stable product radicals might not react efficiently with trapping agents in follow-up reactions, which can result in high radical concentrations that interfere with an indirect kinetic study. Nonetheless, with appropriate control reactions, these clocks can be used in indirect kinetic studies when the trapping agents are

highly reactive as in reactions of tin hydrides or thiols.

Figure 9 shows a number nitrogen-centered radical clocks involving 5-exo cyclizations, and Figure 10 shows nitrogen radical clocks that react by fragmentations. In both figures, appropriate carbon radical clocks are provided that permit comparisons with carbon radical analogs. Aminyl radicals are relatively low reactivity species in addition to alkenes,[42] but fragmentations that produce a relatively stable imine π-bond are fast.[42,43] Protonated dialkyaminium radical cations have long been known to be highly reactive,[44] and Lewis acid complexed aminyl radicals lie between the extremes of the neutral and protonated forms.[45] Amidyl radicals are much more reactive species than α-carbonyl carbon radicals,[46] but iminyl radicals are much less reactive than the carbon analog vinyl radicals.[47] In a predictable manner, phenyl substitution to give the nitrogen equivalents of benzyl radicals results in apparent low reactivity in a cyclopropane-substituted aniline radical cation[48] and in a variety of anilidyl radicals.[49]

Figure 10 Comparisons of nitrogen radical fragmentations to carbon radical reactions. The rate constants are for reactions at room temperature.

4.3 Oxygen Radical Clocks

Oxygen-centered radicals are highly reactive species in comparison to carbon-centered radicals. The archetypal oxygen radical clock reaction is fragmentation of the *tert*-butoxyl radical to give acetone and a methyl radical, which has been studied for half a century.[50] Relative rate constants for competing fragmentation and reaction of the oxyl radical with solvent were reported long ago,[51] and precise absolute rate constants were later determined by LFP methods.[52] Most of the calibrated oxygen radical clocks are fragmentations similar to the *tert*-butoxyl radical reaction,[53–55] but cyclizations,[56] intramolecular hydrogen abstraction,[57] and rearrangements[58] have also been calibrated.

Figure 11 shows examples of oxyl radical clocks. One noteworthy point is that oxygen radical kinetics is sensitive to solvent polarity effects; for example, the rate constant for fragmentation of the *tert*-butoxyl radical in water is more than 100 times greater than that for fragmentation in CCl_4.[52] Another important point is that an oxyl radical ring opening can be reversible, as seen in the cyclopentanoxyl radical,[55] although the carbon-centered radical product is favored thermodynamically.
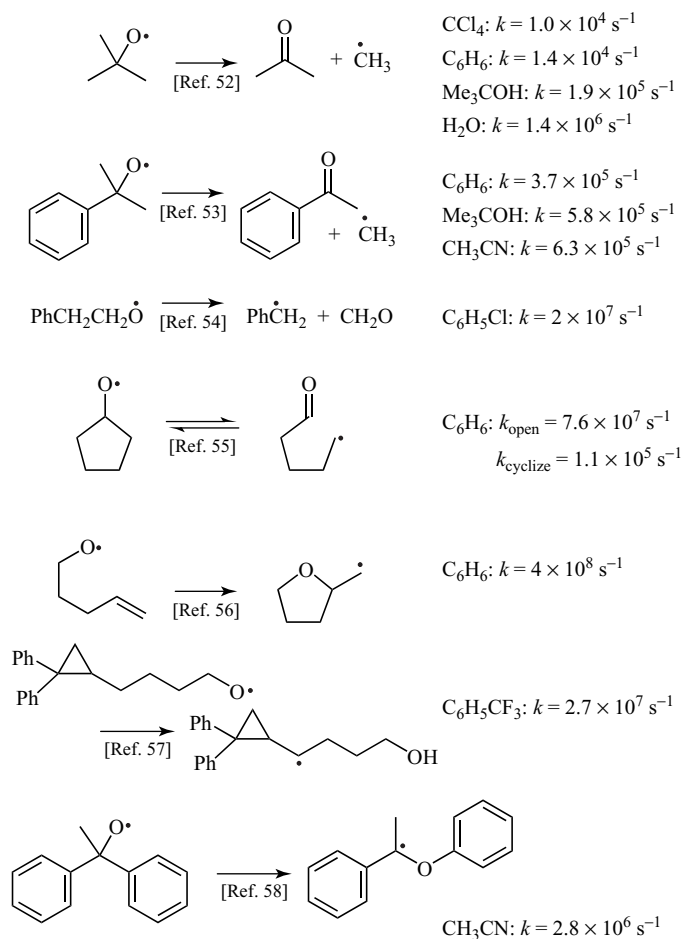
4.4 Acyl Radical Clocks

Fragmentations of acyl radicals give alkyl radicals and carbon monoxide, and these decarbonylation reactions are reversible when conducted at high CO pressure. Several kinetic studies were conducted, and a number of results were collected in an overview published in 1987.[59] Some examples of acyl radical clocks are shown in Figure 12.[60–64] The kinetics of these reactions was obtained over a wide temperature range and should be among the more accurate values available.

5 KINETIC TABLES

Radical reaction rate constants are presented in many of the articles in this encyclopedia in conjunction with the other details of the chemistry of the radicals. In this section, some of the more commonly encountered second-order rate constants are collected for convenient reference. These include rate constants for hydrogen atom transfer reactions from the more common radical reducing agents and addition reactions of carbon-centered radicals to various alkenes.

CCl$_4$: $k = 1.0 \times 10^4$ s^{-1}
C$_6$H$_6$: $k = 1.4 \times 10^4$ s^{-1}
Me$_3$COH: $k = 1.9 \times 10^5$ s^{-1}
H$_2$O: $k = 1.4 \times 10^6$ s^{-1}

C$_6$H$_6$: $k = 3.7 \times 10^5$ s^{-1}
Me$_3$COH: $k = 5.8 \times 10^5$ s^{-1}
CH$_3$CN: $k = 6.3 \times 10^5$ s^{-1}

PhCH$_2$CH$_2$Ȯ $\xrightarrow{\text{[Ref. 54]}}$ PhĊH$_2$ + CH$_2$O   C$_6$H$_5$Cl: $k = 2 \times 10^7$ s^{-1}

C$_6$H$_6$: $k_{\text{open}} = 7.6 \times 10^7$ s^{-1}
$k_{\text{cyclize}} = 1.1 \times 10^5$ s^{-1}

C$_6$H$_6$: $k = 4 \times 10^8$ s^{-1}

C$_6$H$_5$CF$_3$: $k = 2.7 \times 10^7$ s^{-1}

CH$_3$CN: $k = 2.8 \times 10^6$ s^{-1}

Figure 11 Examples of oxygen-centered radical clocks. The rate constants in units of s^{-1} are for reactions at approximately room temperature.

5.1 Hydrogen Atom Transfer Kinetics

Table 4 contains rate constants for the reactions of some of the more commonly employed hydrogen atom transfer reactions. Hydrogen atom transfer reactions of group 14 hydrides and group 16 hydrides are the best characterized radical reactions kinetically, and Table 4 lists values for the most commonly employed reagents.

The most commonly employed radical reducing agent has been tributyltin hydride, Bu$_3$SnH, which has been used extensively for half a century and is the species referred to as *tin hydride*. Triphenyltin hydride, Ph$_3$SnH, is more reactive than Bu$_3$SnH.

Tributylgermanium hydride is somewhat less reactive than Bu$_3$SnH; it can be used in many radical reactions, but it seldom has been. Simple trialkylsilanes such as Et$_3$SiH react too slowly with alkyl radicals to propagate a chain reaction sequence, but the activated silane *tris*(trimethylsilyl)silane, (CH$_3$Si)$_3$SiH, reacts fast enough with carbon radicals to be useful (see **Silanes as Reducing Reagents in Radical Chemistry**, Volume 2). A contemporary review of group 14 hydride reagents and their radical reactions contains the most comprehensive collection of kinetics for these reagents.[14]

For comparisons with the other group 14 hydrides, the rate constants for reactions of the

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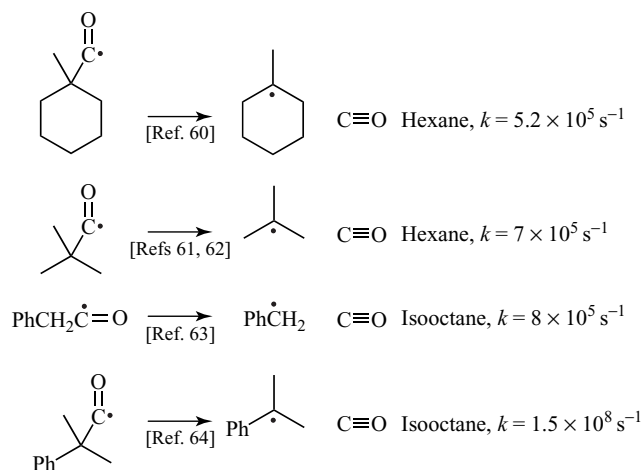
Figure 12 Examples of acyl radical clocks. The rate constants are for reactions at room temperature.

Table 4 Rate constants for hydrogen atom transfer reactions at room temperature.[a]

Radical	$(Me_3Si)_3SiH$	Bu_3SnH	t-BuSH	PhSH	PhSeH
t-BuO$^{\bullet}$	1.1×10^8	2.0×10^8			
$R_2NH^{\bullet+}$		2.4×10^{8b}	3.4×10^{6c}	4.3×10^7	
$RC(O)N^{\bullet}R'$		1.3×10^9		1×10^8	
$R_2N^{\bullet}$	Circa 34[d]	4.3×10^5	6×10^6	1.1×10^8	2×10^9
$R_fCF_2^{\bullet}$	5.1×10^7	2.0×10^8		3×10^5	
$C_6H_5^{\bullet}$	3×10^8	7.8×10^8			
$RCH_2^{\bullet}$	3.9×10^5	2.5×10^6	6×10^6	9×10^7	1.2×10^9
$PhCH_2^{\bullet}$		3.2×10^4		2.8×10^5	
$RC(O)^{\bullet}$	1.8×10^4	3.9×10^5	2×10^{6e}		Circa 4×10^9

[a] Rate constants in units of $M^{-1}\,s^{-1}$ at room temperature unless noted. References: for alkyl radials with group 14 hydrides, Ref. 14; for alkyl radicals with group 16 hydrides, Ref. 33; for aminyl radical, Refs 14, 42; for amidyl radicals, Ref. 46; for benzyl radical, Ref. 65; for fluorocarbon radicals, Ref. 66; for acyl radicals, Refs 14, 67, 68.
[b] For reaction of Ph_3SnH.
[c] For reaction of octanethiol.
[d] 2,2,6,6-tetramethylpiperidine radical.
[e] Reaction with "*tert*-dodecanethiol" at 80 °C.

silane hydrogen of Et_3SiH with *tert*-butoxyl radical and a simple alkyl radical at room temperature are 4.6×10^6 and $3.2 \times 10^2\,M^{-1}\,s^{-1}$, respectively.[14,69,70] Note that the methylene hydrogens in Et_3SiH also are transferred to radicals, resulting in somewhat larger overall rate constants than those quoted here. Also for comparison purposes, Bu_3GeH reacts at room temperature with *tert*-butoxyl and alkyl radicals with rate constants of 9.2×10^7 and $9.5 \times 10^4\,M^{-1}\,s^{-1}$, respectively.[14,70–72] Triphenyltin hydride has been well studied and the rate constants for reactions with many radicals have been collected[14]; Ph_3SnH reacts somewhat faster than Bu_3SnH.

Group 16 hydrides are well-known hydrogen atom donors. Phenols have long been used as inhibitors for spoilage, but thiols are more commonly applied in synthetic applications, and benzeneselenol is a highly reactive trapping agent. Thiols are highly reactive hydrogen atom transfer agents with nucleophilic radicals such as alkyl radicals. Many thiols are readily available, and *tert*-butylthiol rate constants are relatively well

studied. Thiophenol is highly reactive, and benzene-selenol reacts at close to diffusion control at room temperature.[21,25,26,29,30,33,65–67]

The group 16 hydrides are limited to some extent in their applications in that the thiyl and selenyl radicals will not abstract halogen atoms from an alkyl halide radical precursor, although they can be used with the PTOC class of radical precursors developed by Barton and coworkers.[10] Nonetheless, it is possible to use a group 16 hydride as fast radical trapping agents with an alkyl halide radical precursor if a group 14 hydride is added as a sacrificial reductant, a method termed *polarity reversal catalysis*.[73] For example, Et_3SiH and *t*-BuSH can be used in combination to reduce an alkyl halide. The thiol reacts rapidly with the alkyl radical, the thiyl radical thus formed will not react with the alkyl halide but does react with the silane to give a silyl radical, and the silyl radical then reacts efficiently with the alkyl halide. This method was also applied with $(Me_3Si)_3SiH$ as sacrificial reductant in a calibration of rate constants for a collection of thiols reacting with alkyl and acyl radicals.[68] In a similar manner, one can generate PhSeH *in situ* by reaction of PhSeSePh with Bu_3SnH and use the combination of the diselenide and tin hydride as an efficient reducing agent with alkyl halide radical precursors.[74] In passing, one should note that chalcogenide (or pseudohalide) radical precursors such as RSPh or RSePh can be contaminated with impurities of dichalconides PhSSPh and PhSeSePh, respectively, which are reduced by Bu_3SnH to give the highly reactive hydrides PhSH and PhSeH; thus, it is possible to generate a highly reactive radical reducing agent unintentionally when pseudohalide radical precursors are employed.[74]

A new aspect of hydrogen atom transfer to alkyl radicals is evolving at the time of this writing. Owing to the toxicity of tin-containing compounds, chemists have sought "tin-free" alternatives for many years. For example, Derek Barton noted that the family of PTOC ester radical precursors he and his coworkers developed in the 1980s[10] were aimed in part at removing the need for tin hydride in radical applications in synthesis. More recently, there has been progress in using water and simple alcohols as hydrogen atom donors toward radicals. The strong OH bond in water is significantly weakened by complexation with Lewis acids, and water and alcohols complexed with boron species have been shown to react with carbon radicals.[75,76] A kinetic study of the reactions of triethylborane-complexed water and methanol found the rate constants for reactions on the order of $1 \times 10^4 \, M^{-1} \, s^{-1}$ at room temperature,[77] but an unusual entropic term was found, indicating that an equilibration preceded the rate-determining hydrogen atom transfer step. Recently, Renaud and coworkers (private communication from Dr. G. Povie for results from G. Poive, M. Marzorati, P. Bigler, and P. Renaud) found that the equilibrium constant for binding water and Et_3B was quite small at room temperature, a result consistent with the unusual entropic term obtained in the kinetic studies. This observation suggests that the measured rate constant for hydrogen atom transfer reactions of Et_3B complexed water and alcohols might be only a small fraction of the true rate constant, which might be nearly as great as that for tin hydride. One is encouraged to refer to contemporary studies reported after this review was written for recent progress in this area.

5.2 Additions to Alkenes

The rates of reactions of radicals with alkenes provides insight into the reactivities of the radicals and the substrates. A large collection of background data was accumulated by the late Hans Fischer and coworkers who studied reactions of radicals that can be classified as nucleophilic (α-oxygen substituted),[78] electrophilic (α-ester substituted),[79] and mixed (ambiphilic, alkyl)[80] reactivity. Table 5 contains collections of data that show the reactivities of various radicals with different alkenes. The table includes data from Dolbier and coworkers for reactions of the perfluoropropyl radical.[81]

A relative complete collection of rate constants for reactions of alkyl radicals with other unsaturated substrates is collected in Table 6.[82–87] This data is presented in terms of relative rate constants because it was derived from both inter- and intramolecular reactions. It can be used as a predictor of radical reactivity for a given substrate in reactions with alkyl radicals and possibly other nucleophilic radicals, but one must be cautious about using this table for electrophilic radicals such as alkoxyl or perfluroalkyl radicals.

Table 5 Rate constants for addition reactions of radicals to substituted alkenes at room temperature.[a]

	$CH_2{=}CHOEt$	$CH_2{=}CHR$	$CH_2{=}CHCO_2Me$	$CH_2{=}CHPh$
$(CH_3)_2C(OH)^\bullet$	32	1.1×10^3	$>1 \times 10^7$	2.2×10^6
$H_3C^\bullet$	1.4×10^4	7.6×10^3	3.4×10^5	2.6×10^5
$t\text{-}BuO_2CCH_2^\bullet$	1.5×10^2	54	4.9×10^2	1.9×10^3
$C_3F_7^\bullet$		6.2×10^6	2.2×10^{6b}	4.3×10^7

[a] Reactions at room temperature, rate constants in units of $M^{-1}\,s^{-1}$. Data from Refs 78–81.
[b] Substrate was acrylonitrile.

Table 6 Relative rate constants for additions of alkyl radicals to unsaturated substrates at room temperature.[a]

Substrate	Relative k	References
$RCH{=}CH_2$	1.0	
$R{-}C{\equiv}CH$	0.075	82
$R{-}C{\equiv}N$	0.025	82
$RCH{=}O$	0.56	83
$RCH{=}NR$	3.75	84
$C{\equiv}O$	18	85
$RCH{=}NOCH_3$	24	86
$RCH{=}NNR_2$	39	86
$CH_2{=}CHCH_2Si(CH_3)_3$	40	87

[a] Relative rate constant at room temperature determined by comparing kinetics of pairs of inter- or intramolecular reactions.

5.3 Radical Fragmentation Reactions

Radical fragmentations display kinetic effects that are similar to those observed in radical additions. The stability of the incipient radical center is the dominant feature in the kinetics for a series of fragmentations. Table 7 contains rate constants for a series of cyclopropylcarbinyl ring opening reactions that are collected from various sources.[12,28,29,33,88–91] The entropic terms are quite similar for these reactions, and the enthalpic terms provide the major effects on the kinetics. For the series of radical center-substituted cyclopropylcarbinyls, the rate constants are similar except in the case of the highly stabilized benzyl radical. On the other hand, the rate constants for the series of cyclopropylcarbinyl radicals that give substituted product radicals vary widely.
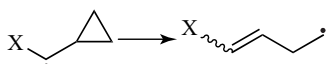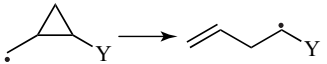
6 CONCLUSION

This overview of radical kinetics is intended to provide a foundation for designing indirect kinetic studies and the application of radical clocks in addition to background kinetic information on some of the more common radical reactions. Kinetic information is an integral part of the description of any radical reaction, and much kinetic information is presented in this encyclopedia in the specific articles describing various types of radicals. Radical kinetic studies have been a focus of interest for many years, and kinetic results fill volumes. Nonetheless, one should appreciate that most radical-based synthetic methods were developed without complete knowledge of absolute rate constants, which highlights the importance of a qualitative understanding of radical kinetics and reactivities.

Table 7 Rate constants for cyclopropylcarbinyl radical fragmentations.[a]

X	$k\,(s^{-1})$	Y	$k\,(s^{-1})$
H	7×10^7	H	7×10^7
CH_3	4×10^7	CH_3	1×10^8
OCH_3	2×10^7	OCH_3	1×10^9
$CO_2CH_2CH_3$	2×10^8	CO_2CH_3	7×10^{10}
Ph	6×10^4	Ph	1.5×10^{11}

[a] Rate constants in units of s^{-1} for reactions at room temperature. Data from Refs 12, 28, 29, 33, 88–91.

ACKNOWLEDGMENTS

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Abstract: An overview of radical kinetics is presented, with an emphasis on competition kinetic methods that can be achieved in most laboratories without special equipment. Methods for indirect studies are described. Collections of various radical clocks that can be used in competition kinetic studies and their rate constants are presented. Kinetic tables for some of the more common radical reactions include those for hydrogen atom transfers from group 14 and group 16 hydrides to radicals, additions of radicals to substituted alkenes and other unsaturated systems, and fragmentations of substituted carbon radicals.

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