

Radical Kinetics as a Mechanistic and Analytical Tool*

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Thermal and photochemical methods for the generation of free radicals, and the kinetics of radical reactions with organic, inorganic and organometallic substrates are discussed. Both direct and competition kinetic methods are described. The latter are based on either product analysis or the kinetic effect of the substrate on the rate of disappearance of the radical precursor. Direct measurements often utilize kinetic probes, some of which are stable free radicals. A method for the generation of sulfur radicals from carbon radicals and thiols, and several reactions of sulfur radicals are also described.

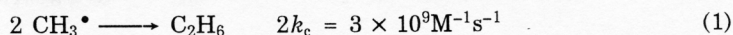
INTRODUCTION

Radicals are involved in such diverse processes as oxidations, catalysis, biological reactions and organic and organometallic synthesis.¹⁻³ The aging processes in humans and various diseases have also been linked to these short-lived, but extremely reactive species.²

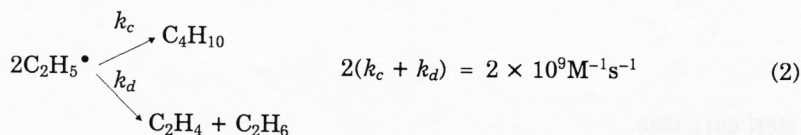
The research in free radical chemistry is truly interdisciplinary, and has brought together inorganic, organic, physical and polymer chemists, photochemists, biologists and medical researchers. Consequently, a variety of methods have been developed and employed for the generation, identification and studies of reactivity of free radicals. They include pulse and γ -radiolysis and a number of photochemical and thermal methods. This review will concentrate on the chemistry of radicals generated by thermal and photochemical methods in aqueous solution.

FREE RADICALS IN SOLUTION

Most of the radicals are short-lived in solution even in the absence of reactive substrates owing to the rapid⁴ self-reactions, combination (dimerization) and disproportionation, that result in the formation of stable products, eq. 1 and 2.

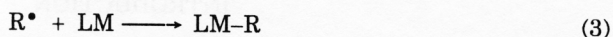


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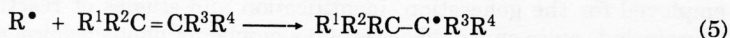


The relative importance of the two pathways varies greatly with the nature of radicals. Combination is favored for the methyl (no disproportionation observed) and other primary alkyl radicals. Disproportionation becomes increasingly important in the series *primary* < *secondary* < *tertiary*. The proportions of the two pathways are constant for a given radicals, and thus the product ratio [dimer]/[disproportionation products] serves as a test for radicals in systems that are free of additional competing reactions with substrates. For ethyl radicals the ratio k_d/k_c , defined as $[\text{C}_2\text{H}_4]/[\text{C}_4\text{H}_{10}]$, is 0.35 ± 0.04 .⁵ This ratio, along with other tests, has been used as evidence for ethyl radical involvement in some reactions.⁶

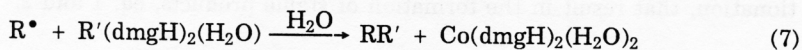
The presence of an unpaired electron renders radicals reactive towards a number of substrates. Electron-transfer reactions cover both oxidations and reductions. Related to radical coupling are reactions with reduced transition metal ions that possess unpaired electrons and are therefore radical species themselves. These reactions yield organometallic complexes, eq. 3, where L represents all the non-alkyl ligands such as $(\text{H}_2\text{O})_5$ or $[(\text{H}_2\text{O})(\text{macrocycle})]$, and charges are omitted. However, at least formally, reaction 3 can also be considered a redox reaction with the metal undergoing a one-electron oxidation. Molecular oxygen, which is a diradical, reacts similarly and yields $\text{ROO}\cdot$, eq. 4.



Reactions with olefins, eq. 5, are the basis of many industrially important olefin polymerization processes.³



Atom abstraction reactions, such as those with alkyl halides,⁷ eq. 6, or with halo- and alkyl-metal complexes,⁸ eq. 7, typically occur by an $\text{S}_{\text{H}}2$ mechanism.

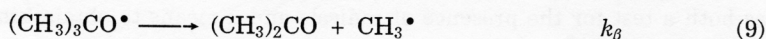
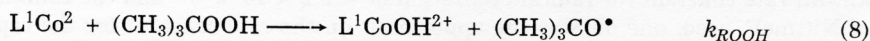


The following chapters describe examples of radical reactions studied by both direct and competition methods. The latter are based on the product analysis and on the effect of added substrates on the kinetics of disappearance of the radical precursor.

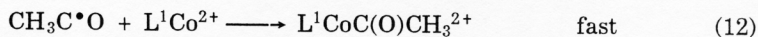
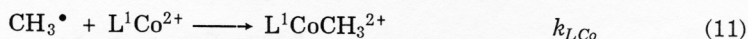
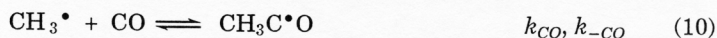
THERMAL GENERATION OF RADICALS
AND COMPETITION KINETICS

Reduction of Alkyl Hydroperoxides

The reactions of alkyl hydroperoxides with reduced metal complexes yield alkoxy radicals, which undergo β -scission and produce alkyl radicals and a ketone. This method of radical generation was used recently⁹ to determine the rate constant for the reaction of methyl radicals with CO. The reaction yields acetyl radicals, $\text{CH}_3\text{C}\cdot\text{O}$, and had been reported¹⁰ to be fast in aqueous solution, but a kinetic study of the gas phase¹¹ reaction yielded a rate constant of only $6.5 \times 10^3 \text{M}^{-1}\text{s}^{-1}$. This controversy has been resolved by a competition study based solely on product distribution.⁹ Methyl radicals were produced in the sequence of reactions 8–9. The reduction of *tert*-BuOOH by a macrocyclic cobalt(II) complex, $(\text{H}_2\text{O})_2\text{CO}([\text{14}] \text{aneN}_4)^{2+}$ (hereafter L^1Co^{2+} , Figure 1) yields *tert*-butoxy radicals, which undergo β -scission ($k_\beta = 1.4 \times 10^6 \text{s}^{-1}$)¹² and yield methyl radicals and acetone.



The competitive reactions of methyl radicals with CO and L^1Co^{2+} yield acetyl radicals and the methylcobalt complex,¹³ respectively, eq. 10–11. Acetyl radicals are rapidly scavenged by L^1Co^{2+} , eq. 12, such that the sequence 10–12 produces two different organocobalt complexes whose yields depend on the values of the rate constants k_{CO} and k_{LCo} and concentrations of CO and L^1Co^{2+} .



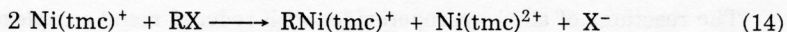
Experiments were conducted in acidic CO-saturated solutions with $[\text{L}^1\text{Co}^{2+}]_0 = (3\text{--}10) [\text{tert-BuOOH}]_0$. Under these conditions eq. 13 holds and k_{CO} is the only unknown.

$$[\text{L}^1\text{CoC}(\text{O})\text{CH}_3^{2+}]_\infty = - (k_{\text{CO}}[\text{CO}]_{\text{av}}/2k_{\text{LCo}}) \ln \left\{ 1 - \frac{2[(\text{CH}_3)_3\text{COOH}]_0}{[\text{L}^1\text{Co}^{2+}]_0 + (k_{\text{CO}}[\text{CO}]_{\text{av}}/k_{\text{LCo}})} \right\} \quad (13)$$

The experimentally determined yields of $\text{L}^1\text{CoC}(\text{O})\text{CH}_3^{2+}$ were fitted to eq. 13 and yielded $k_{\text{CO}} = 2.3 \times 10^6 \text{M}^{-1}\text{s}^{-1}$. Similar experiments using L^2Co^{2+} ($\text{L}^2 = \text{Me}_6\text{--}[\text{14}] \text{aneN}_4$) gave $k_{\text{CO}} = 1.8 \times 10^6 \text{M}^{-1}\text{s}^{-1}$. Thus the capture of $\text{CH}_3\cdot$ by CO in acidic aqueous solutions takes place with an average rate constant of $(2.0 \pm 0.3) \times 10^6 \text{M}^{-1}\text{s}^{-1}$, approximately 300 times faster than in the gas phase. The difference in polarity between methyl and acetyl radicals is probably responsible for this solvent effect.

Reduction of Alkyl Halides. Cyclization as a Test for Free Radicals

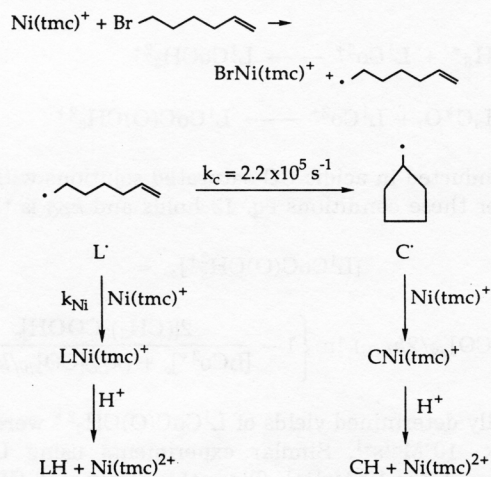
The macrocyclic Ni(I) complex $\text{Ni}(\text{tmc})^+$ (tmc = tetramethylcyclam) reacts with alkyl halides to yield alkylnickel(II) products according to eq. 14.⁶



The 2:1 stoichiometry and the reactivity orders, $\text{CH}_3 < \text{primary alkyl} < \text{secondary alkyl}$, and $\text{Cl} < \text{Br} < \text{I}$, suggest a one-electron radical process. This is strongly supported by the results obtained with a cyclizable probe, 6-bromo-1-hexene,¹⁴ which yielded a mixture of 1-hexene (LH) and methyl-c-pentane (CH), consistent with the mechanism in Scheme 1. The linear hexenyl radical L^\bullet , formed in the rate determining halogen abstraction step, either cyclizes to C^\bullet or reacts with $\text{Ni}(\text{tmc})^+$. The cyclic radical C^\bullet is also captured by $\text{Ni}(\text{tmc})^+$ and yields $\text{CNi}(\text{tmc})^+$. Both alkylnickel complexes hydrolyze within minutes and yield the respective hydrocarbons: $\geq 85\%$ CH (methyl-c-pentane) and $\leq 15\%$ LH (1-hexene). From this product distribution, the known rate constant for radical cyclization ($k_c = 2.2 \times 10^5 \text{ s}^{-1}$)¹⁴ and the concentration of $\text{Ni}(\text{tmc})^+$ used, one obtains the upper limit on the rate constant for the capture of L^\bullet by $\text{Ni}(\text{tmc})^+$, $k_{\text{Ni}} \leq 6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The formation of the cyclic product thus serves as both a test for the presence of radicals and a means to obtain kinetic data for the competing reaction.

Although the formation of cyclic products strongly supports the involvement of radicals, some caution is necessary, especially in nonaqueous solutions, since it has been shown that corresponding carbanions also cyclize.¹⁵

Once the question of one-electron *vs.* two-electron reduction of alkyl halides is settled, the mechanism of the first step in Scheme I can be analyzed in even more detail. Specially, does the reaction take place by an outer-sphere (electron-transfer) or inner-sphere

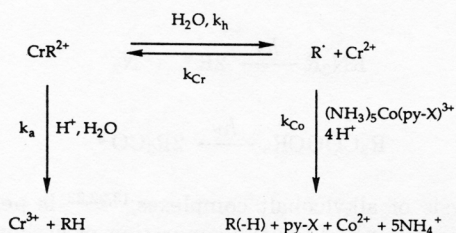


Scheme I. Detailed mechanism of the reaction of hexenyl bromide with $\text{Ni}(\text{tmc})^+$ (tmc = tetramethylcyclam).

(halogen atom transfer) process? Because of the substitutional lability of Ni(II), product analysis is not useful in distinguishing between the two mechanisms. The issue was resolved by noting that a related strongly reducing, but sterically crowded Ni(dmc)⁺ (dmc = decamethylcyclam) reacts with alkyl halides much more slowly¹⁶ than Ni(tmc)⁺ does. This observation supports a bridged transition state, *i.e.* an inner sphere mechanism which is not easily accessible to the sterically encumbered complex.

Thermal Homolysis

Transition metal-carbon bonds are cleaved both thermally and photochemically to yield carbon-centered radicals and reduced metal complexes, according to the reverse of eq. 3. The thermal reaction is a convenient source of radicals for competition studies. Consider a system consisting of a homolyzing organometallic complex and a substrate that reacts with the radical, but not with the reduced metal LM or with the radical precursor LM-R. The reaction of pyridine complexes of Co(III) with $\bullet\text{C}(\text{CH}_3)_2\text{OH}$, using $(\text{H}_2\text{O})_5\text{CrC}(\text{CH}_3)_2\text{OH}^{2+}$ as a radical precursor, Scheme II, illustrates this case.¹⁷



Scheme II

The organochromium complex reacts in two parallel reactions: reversible homolysis to Cr^{2+} and $\bullet\text{C}(\text{CH}_3)_2\text{OH}$, and irreversible hydrolysis to Cr^{3+} and $(\text{CH}_3)_2\text{CHOH}$. The rate law for the disappearance of $\text{CrC}(\text{CH}_3)_2\text{OH}^{2+}$ is given in eq. 15, and its linearized form in eq. 16. The hydrolysis rate constant was determined independently under the conditions of large $[\text{Cr}^{2+}]$ which makes the homolytic path unproductive.

$$\frac{-d[\text{CrR}^{2+}]}{dt} = k_a + \left(\frac{k_h k_{Co} [(\text{NH}_3)_5\text{Co}(\text{py-X})^{3+}]}{k_{Cr} [\text{Cr}^{2+}] + k_{Co} [(\text{NH}_3)_5\text{Co}(\text{py-X})^{3+}]} \right) [\text{CrR}^{2+}] \quad (15)$$

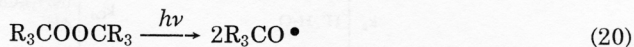
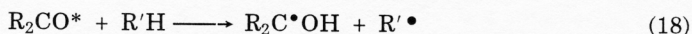
$$\frac{1}{k_{obs} - k_a} = \frac{1}{k_h} + \frac{k_{Cr}}{k_h k_{Co}} \left(\frac{[\text{Cr}^{2+}]}{[(\text{NH}_3)_5\text{Co}(\text{py-X})^{3+}]} \right) \quad (16)$$

The appropriate plot or the numerical fitting of the data yield the values of $k_{Cr}/k_h k_{Co}$ and $1/k_h$. With two of the rate constants known, $k_h = 0.127 \text{ s}^{-1}$ ¹⁸ and $k_{Cr} = 5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$,¹⁹ one calculates the third, $k_{Co} = 3.4 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ (py-4-N(CH₃)₂), 8.7×10^6 (py-4-C(CH₃)₃), 9.3×10^6 (py-4-CH₃), 1.2×10^7 (py), 3.1×10^7 (py-3-Cl) and 1.42×10^8 (py-3-CN). Linear free energy correlations were employed to establish the

mechanism for this reaction as an outer-sphere electron transfer to cobalt, and to rule out the attack of the radical on the pyridine ring.^{17a} Reactions of $\bullet\text{C}(\text{CH}_3)_2\text{OH}$ with Ru(II) ammine complexes, $\text{Ti}(\text{H}_2\text{O})_6^{3+}$, TiO^{2+} , and Cr(III) pyridine complexes have also been studied by similar methods.^{17b-d}

PHOTOCHEMICAL GENERATION OF RADICALS

The UV photolysis of a large number of organic and organometallic compounds yields radicals either directly or in subsequent rapid reactions of excited states with appropriate substrates. Hydrogen abstraction by triplet ketones yields the ketone- and substrate-derived radicals, eq. 17–18.²⁰ Diazo compounds yield radicals directly and *via* $\text{N}_2\text{R}^\bullet$, eq. 19,²¹ whereas alkyl peroxides and hydroperoxides yield alkoxy radicals, eq. 20, which are then rapidly converted to ketones and alkyl radicals, as shown for $(\text{CH}_3)_3\text{CO}^\bullet$ in eq. 9.



The visible photolysis of alkylcobalt complexes,^{13,22,23} is perhaps the most comprehensive and convenient method for the generation of carbon-centered radicals in aqueous solution for both steady state and flash photolysis studies, eq. 21. This method makes it possible to produce a large variety of radicals, which allows systematic studies of radical reactions to be carried out.



The readily available alkylcobaloximes²⁴ ($\text{RCo}(\text{dmgH})_2\text{B}$, $\text{R} = \text{CH}_3$, *primary*, *secondary*, *phenyl*, *allyl*, *aralkyl*, and $\text{B} = \text{pyridine}$, H_2O , PR_3 *etc.*) and alkylcobalt(cyclam) complexes^{13,23} ($\text{RCo}([\text{14}] \text{aneN}_4)(\text{H}_2\text{O})^{2+}$, $\text{R} = \text{primary}$ and substituted primary alkyl), Figure 1, have been used most extensively. The extreme chemical inertness of the latter series makes these complexes compatible with a large number of interesting substrates.

KINETICS BY LASER FLASH PHOTOLYSIS AND USE OF KINETIC PROBES

The kinetics of radical reactions with a number of reagents have been studied by laser flash photolysis using either of the two organocobalt series as the source of radicals. Radical concentrations have to be kept low (1–2 μM) in such experiments to prevent losses and complications caused by radical self-reactions. Thus the optical absorbance changes in reactions with most substrates are too small for direct monitoring and require the use of kinetic probes,^{14c,25} *i.e.* molecules that react rapidly with radicals

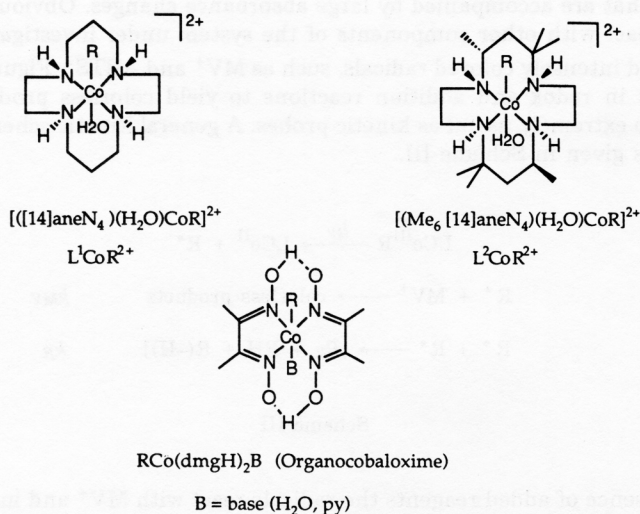


Figure 1. Structures of some alkylcobalt complexes

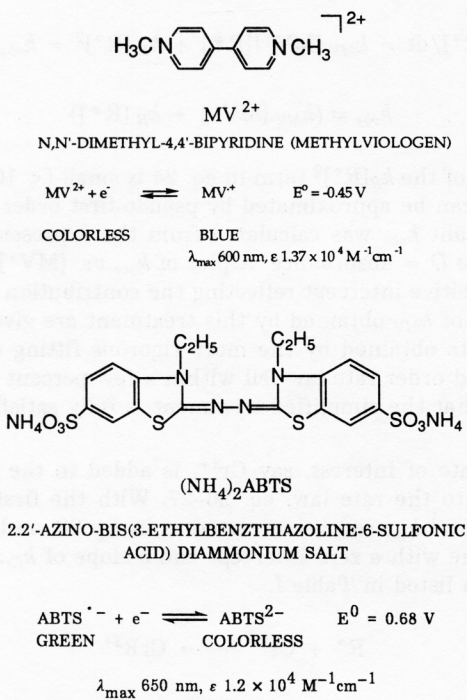
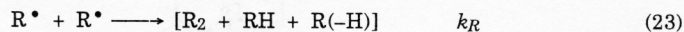
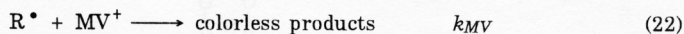


Figure 2. Structures and properties of the kinetic probes MV^{2+} and $ABTS^{2-}$.

in reactions that are accompanied by large absorbance changes. Obviously, the probes should not react with other components of the system under investigation.

Stable and intensely colored radicals, such as MV^+ and $ABTS^-$, Figure 2, react with alkyl radicals in redox and addition reactions to yield colorless products and have proved²⁶ to be extremely useful as kinetic probes. A general kinetic scheme, using MV^+ as example, is given in Scheme III.



Scheme III

In the absence of added reagents the radicals react with MV^+ and in self-reactions, eq. 22 and 23. MV^+ was typically used in at least 10-fold excess over the radical, and the reaction was monitored at 600 nm, an absorption maximum of MV^+ ($\epsilon = 1.37 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$).²⁷ The rate law is given in eq. 24 and 25.

$$-d[R^\bullet]/dt = k_{MV}[MV^+][R^\bullet] + k_R[R^\bullet]^2 = k_{obs}[R^\bullet] \quad (24)$$

$$k_{obs} = (k_{MV}[MV^+] + k_R[R^\bullet]) \quad (25)$$

The contribution of the $k_R[R^\bullet]^2$ term in eq. 24 is small (< 10%) such that the data for each experiment can be approximated by pseudo-first order kinetics. The pseudo-first order rate constant k_{obs} was calculated from the expression $(D_t - D_\infty) = (D_0 - D_\infty) \exp(-k_{obs}t)$, where D = absorbance. A plot of k_{obs} vs. $[MV^+]$ is linear with a slope of k_{MV} and a small positive intercept reflecting the contribution from the second term in eq. 25. The values of k_{MV} obtained by this treatment are given for several radicals in Table I. The results obtained by the more rigorous fitting of kinetic data to the mixed first and second order rate law fell within a few percent of the values listed in Table I, confirming that the simplified treatment is fully satisfactory under the conditions employed.

When the substrate of interest, say Cr^{2+} , is added to the system, an additional term is introduced into the rate law, eq. 26–27. With the first two terms in eq. 27 known, the experimental k_{obs} can be corrected as in eq. 28, and a plot of k_{corr} against $[Cr^{2+}]$ is a straight line with a zero intercept and a slope of k_{Cr} . The values of k_{Cr} for some radicals are also listed in Table I.



$$k_{obsd} = k_{MV}[MV^+] + k_R[R^\bullet] + k_{Cr}[Cr^{2+}] \quad (27)$$

$$k_{corr} = k_{obs} - k_{MV}[MV^+] - k_R[R^\bullet] = k_{Cr}[Cr^{2+}] \quad (28)$$

TABLE I

Rate Constants ($10^{-9}M^{-1}s^{-1}$) for the reactions of selected carbon-centered radicals with MV^+ , $ABTS^-$ and $(H_2O)_6Cr^{2+}$ ^a

| Radical | MV^+ | $ABTS^-$ | $(H_2O)_6Cr^{2+}$ |
|-------------|--------|----------|-------------------------|
| CH_3 | 1.2 | 1.2 | 0.22, 0.24 ^b |
| C_2H_5 | 1.0 | 1.1 | 0.19 |
| C_3H_7 | 1.2 | 1.2 | 0.22 |
| $2-C_3H_7$ | 1.2 | 1.4 | |
| CH_2OCH_3 | 1.1 | 1.8 | 0.23 |
| CH_2Cl | 1.4 | 1.2 | 0.24 |
| CH_2Br | 2.1 | 2.0 | 0.22 |
| $c-C_5H_9$ | 0.91 | 1.2 | 0.080 ^c |
| CH_2Ph | 1.2 | 1.2 | 0.085 ^d |

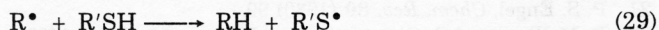
^a In acidic aqueous solutions at 25 °C. Data are from references 26a, 29 and 30. ^b A. Sauer, H. Cohen, and D. Meyerstein, *Inorg. Chem.* **27** (1988) 4578. ^c J. H. Espenson, P. Connolly, D. Meyerstein, and H. Cohen, *ibid.* **22** (1983) 1009. ^d R. J. Blau, J. H. Espenson, and A. Bakač, *ibid.* **23** (1984) 3526.

The same method, using either MV^+ or $ABTS^-$ as probes, was used to determine rate constants for the reactions of radicals with several cobalt(II) macrocyclic complexes, ^{26b} $V(H_2O)_6^{2+}$, ²⁸ $Cr([15]aneN_4)(H_2O)_2^{2+}$, ²⁹ $Ni(cyclam)^{2+}$, ³⁰ and O_2 .³¹

Radical probes are also important as analytical reagents for transient radicals. The second term in eq. 25 becomes negligible when the concentration of the probe is sufficiently high. The reaction of the probe with the radicals is then quantitative and the absorbance changes in the kinetic experiments yield directly the concentration of R^\bullet produced in the flash.

CARBON RADICALS AS A SOURCE OF HETEROATOM RADICALS

Thiyl radicals, RS^\bullet , play important roles in biological and bioinorganic reactions, as well as in the chemistry of coal and atmospheric pollution.³² Early kinetic research has relied heavily on pulse radiolysis, but recently a much more accessible photochemical method was developed.³³ It is based on the reaction of C-centered radicals with thiols, eq. 29. The ~40 kJ/mol difference between the C-H and S-H bond energies makes this reaction thermodynamically favorable. In fact, reaction 29 is the basis of free radical repair in biological systems.³²



The radical R^\bullet (usually CH_3^\bullet) was generated by laser flash photolysis of $(H_2O)([14]aneN_4)CoR^{2+}$ in the presence of thiols. Both reactions 29 and subsequent reactions of thiyl radicals take place with little absorbance change and radical probes $ABTS^{2-}$ and $TMPD$ (tetramethylphenylenediamine) were employed in the kinetic studies. The rate constants for reaction 29 cover a rather narrow range, $(3-50) \times 10^7 M^{-1}s^{-1}$, for a number of radicals and thiols.³⁴ Thiyl radicals, on the other hand, are quite selective and the values of the rate constants for the reactions with transition

metal complexes cover many orders of magnitude. This includes electron transfer as well as metal-sulfur bond forming reactions.³⁴

Thiyl radicals react with organometallic complexes, such as L^1CoR^{2+} , in bimolecular substitutions and hydrogen abstraction reactions. Interestingly, thiyl radicals are much more effective than alkyl radicals in abstracting hydrogen atoms from organometallic complexes,³⁵ possibly because of the greater polarizability of thiyl radicals.^{35,36}

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SAŽETAK

Kinetika radikala u analitici i određivanju mehanizama reakcija

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Dan je prikaz toplinskih i fotokemijskih metoda za pripremu slobodnih radikala. Opisane su izravne i kompeticijske metode za mjerenje brzine reakcija radikala s organskim, anorganskim i organometalnim spojevima. Kompeticijske metode osnivaju se na analizi produkata i na kinetičkom efektu supstrata na brzinu nestajanja izvora radikala. U izravnima kinetičkim mjerenjima često se koriste kinetički indikatori među kojima posebno mjesto zauzimaju postojani radikali. Opisana je i metoda za pripremu sumpornih radikala iz ugljikovih radikala i tiola, kao i neke nove reakcije sumpornih radikala.