Peroxyl Radicals

8.1
General Remarks

Dioxygen, O_2, is omnipresent in our environment. Its solubility in water is 1.35×10^{-3} mol dm^{-3} at 20 °C (air-saturated: 2.8×10^{-4} mol dm^{-3}), and at 37 °C it drops to 77% of these values. Most experiments that are reported in the literature to have been carried out under ambient conditions will contain that much O_2. However, as a free-radical-induced reaction continues to proceed it is likely to consume O_2, and due to the low prevailing O_2 concentration it may become consumed before the reaction has been stopped. This can lead to considerable artifacts.

It is often assumed that the O_2 concentration in a cellular environment is the same as that in dilute aqueous solution. This assumption does not seem to be correct, not only because O_2 may be consumed by metabolic processes, and its rediffusion to the target site, e.g. to the nucleus, may be too slow to replenish the O_2 concentration to saturation level. More importantly, the solubility of O_2 in such highly concentrated solutions of proteins and nucleic acids that prevail in the nucleus is extremely low, that is, only a small fraction of that in water (Zander 1976a,b).

In radiobiology, O_2 has a sensitizing effect on cell survival and other parameters (Chap. 12.11). Moreover, the superoxide radical, $O_2^{\bullet-}$, may trigger important cellular reactions (although many of its reactions are slow; for a review see Bielski and Gebicki 1970). For example, there is increasing evidence that $O_2^{\bullet-}$ may play a role in the intercellular induction of apoptosis (Bauer 2000; Engelmann et al. 2000; Herdener et al. 2000).

8.2
Kinetics of the Reaction of Free Radicals with Oxygen

Details of the formation and decay of peroxyl radicals in an aqueous environment have been reviewed in some detail (von Sonntag and Schuchmann 1991, 1997; Schuchmann and von Sonntag 1997), and its suffices here to report only the most important points.

Most organic radicals react practically irreversibly with O_2 at close to diffusion-controlled rates (typically at 2×10^9 dm^3 mol^{-1} s^{-1}), and in air-saturated aqueous solutions the lifetime of these radicals will only be ~2 µs [reaction (1); for a compilation of rate constants see Neta et al. 1990].

$$R^{\bullet} + O_2 \rightleftharpoons RO_2^{\bullet} \tag{1}$$

Not all encounters in the reaction of O_2 with e_{aq}^- lead to $O_2^{\bullet-}$, and the appropriate spin factor for this is 2/3 because of the large zero-field splitting of triplet O_2 (Schmidt et al. 1995). Similarly, spin dephasing is observed for the reaction of $H^{\bullet}$ with O_2 (Han and Bartels 1994), and this may apply also to other $R^{\bullet}$ plus O_2 reactions.

The R-OO$^{\bullet}$ BDEs for alkylperoxyl radicals are around 125 kJ mol^{-1}, for vinyl- and aryl-type peroxyl radicals they are even higher by about 63 kJ mol^{-1} (Kranen-

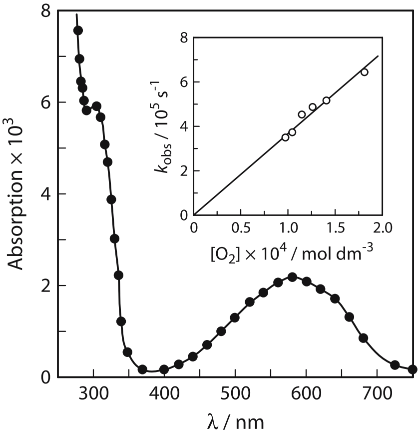


Fig. 8.1. Pulse radiolysis of Ar/O_2 (9:1)-saturated aqueous solution of tetrachloroethene. Absorption spectrum of the trichlorovinylperoxyl radical taken after completion of the reaction. *Inset* Rate of buildup of the trichlorovinylperoxyl radical as a function of the O_2 concentration. (Source: Mertens and von Sonntag 1994, with permission)

burg et al. 2000). Only for the cyclohexadienyl radical, it is as low as 25 kJ mol^{-1}, and this leads to noticeable reversibility (for DFT calculations see Naumov and von Sonntag 2005). For the related pentadienylperoxyl radical a BDE of 56 kJ mol^{-1} has been determined for the gas phase (Zils 2000; Zils et al. 2001).

As a rule of thumb, peroxyl radicals absorb at shorter wavelength and have lower and less structured absorptions than their parent radicals. There are only a few exceptions: vinyl- and phenyl-type peroxyl radicals (Alfassi et al. 1994, 1995; Mertens and von Sonntag 1994; Fang et al. 1995b; Khaikin and Neta 1995) as well as thiylperoxyl radicals (Jayson et al. 1971; Tamba et al. 1986; Zhang et al. 1994) absorb in the near UV and visible, cf. Fig. 8.1, while their parent radicals have barely any absorption in the wavelength region of interest (for a quantum-chemical study of peroxyl radical absorption spectra see Naumov and von Sonntag 2005).

In the present context of nucleic acid free-radical chemistry, such a strong absorption in the visible of a vinylic peroxyl radical is observed in the case of the uracil-5-peroxyl radical (λ_{max} = 570 nm; Mertens and von Sonntag 1994) which plays a role in the free-radical chemistry of 5BrUra.

When the C-OO$^•$ bond is weak, the R$^•$ + O_2/ROO$^•$ system becomes reversible (k_{-1} now being quite fast). To date, examples of reversibility at room temperature has only been found for pentadienyl-type radicals (Chan et al. 1978; Pan and von Sonntag 1990; Pan et al. 1993; Fang et al. 1995a). Such radicals are formed, when a pentadienylic hydrogen is abstracted from polyunsaturated fatty acids or when $^•$OH adds to aromatic compounds (forming hydroxycyclohexadienyl radicals). Hydroxycyclohexadienyl radicals absorb strongly near 310 nm (325 nm in the case of the one derived from anisole, Fig. 8.2), while the corresponding peroxyl radicals absorb only weakly at this wavelength. Due to the reversibility of the re-

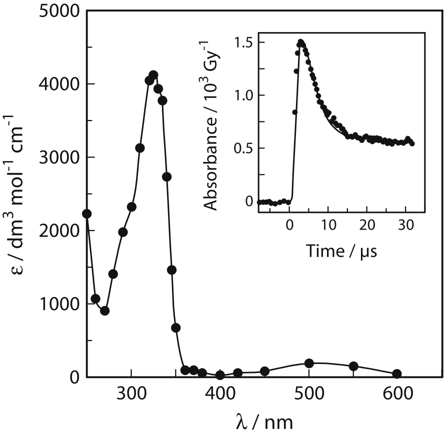


Fig. 8.2. Pulse radiolysis of N_2O-saturated aqueous solutions of anisole. Spectrum of the anisole-derived hydroxycyclohexadienyl radicals. *Inset* shows their decay in the presence of 15% O_2 and formation of the "plateau". (Source: Fang et al. 1995a, with permission)

action, the absorbance of the hydroxycyclohexadienyl radicals does not decay to the low level that would be given by the absorption of the remaining hydroxycyclohexadienylperoxyl radicals alone, but settles a higher "plateau" value (Fig. 8.2, inset). The height of this "plateau" decreases with increasing O_2 concentration.

Subsequent to the rapid attainment of this near-equilibrium situation, the radicals decay more slowly by both unimolecular and bimolecular processes (discussed below). For this simple case, it can be shown that when the decay process is much slower than the rates of the forward and reverse reactions, the observed rate constant for the disappearance of $R^\bullet$ is given by the expression $k_{obs} = k_{forward}[O_2] + k_{reverse}$. When k_{obs} of the decay of the hydroxycyclohexadienyl radicals is plotted as a function of the O_2 concentration, the slope represents the rate constant of the forward reaction, and the intercept that of the reverse reaction (Fig. 8.3).

Stability constants of a number of differently substituted hydroxycyclohexadienyl peroxyl radicals have been obtained from such data (for a compilation see von Sonntag and Schuchmann 1997).

The thiyl/thiylperoxyl radical system is also reversible [reaction (2); Tamba et al. 1986; Zhang et al. 1994], although the thiylperoxyl radicals are stabilized by an intramolecular charge transfer (Razskazovskii et al. 1995). The evaluation of the equilibrium constant is not straightforward because the thiylperoxyl radical undergoes a thermal but also a light-induced (Sevilla et al. 1990a) rearrangement into the much more stable sulfonyl radical [reaction (3)] which is subsequently converted into the corresponding peroxyl radical [reaction (4)]. In addition, equilibrium (5) has to be taken into account, although this equilibrium lies largely on the side of the thiyl radical (Zhang et al. 1994; for DFT calculations see Naumov and von Sonntag 2005).

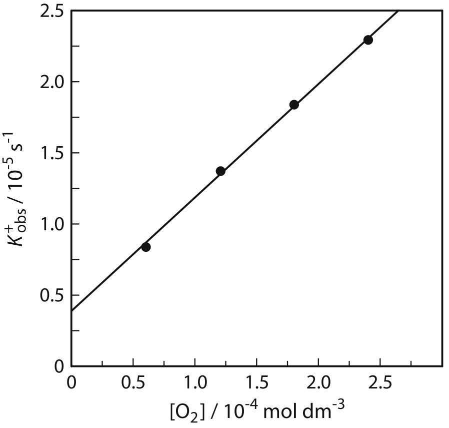
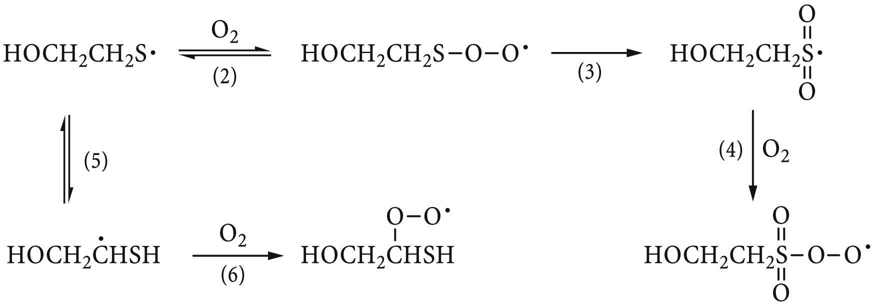


Fig. 8.3. Pulse radiolysis of N_2O-saturated aqueous solutions of anisole. Plot of the rate of the decay of the anisole-derived hydroxycyclohexadienyl radicals as a function of the O_2 concentration. (Source: Fang et al. 1995a, with permission)

While most carbon-centered radicals react fast or at least reversibly with O_2, some highly conjugated radicals that have considerable spin density at a heteroatom do not react with O_2 (for the reactions of heteroatom-centered radicals with O_2, see Schuchmann and von Sonntag 1997). Typical examples are the phenoxyl radicals (Hunter et al. 1989; Jin et al. 1993) and the vinylogs of phenoxyl radicals (Benjan et al. 2001). They only show some reactivity when the electron density in the ring is increased by electron donating substituents (Wang et al. 1994). Other examples are the tryptophan-derived radical (Fang et al. 1998) and, most relevant to DNA, the guanyl radical, $G^{\bullet}$ (von Sonntag 1994).



8.3

Geometries, Spin Densities, Oxidative Power and pK_a Values of Peroxyl Radicals

Equilibrium geometries, harmonic vibrational frequencies, dipole moments and hyperfine couplings for a series of peroxyl radicals have been calculated by an ab initio method (Besler et al. 1986). The spin density of ^{17}O-enriched peroxyl radicals correlates well with the Taft substituent parameter σ* and the ET rate with strong reductants (Sevilla et al. 1990b; for a theoretical study see Raiti and Sevilla 1999; for further studies on the reduction of peroxyl radicals see Packer et al. 1980; Alfassi et al. 1987; Asmus et al. 1988; Schuchmann and von Sonntag 1988; Neta et al. 1989; El-Agamey and McGarvey 2002). The redox potential of simple alkylperoxyl radicals is $E^7 = 0.77$ V; it is substantially increased by electron-withdrawing substituents [$E^7(CCl_3OO^{\bullet}) = 1.15$ V, $E^7(RC(O)OO^{\bullet}) = 1.6$ V; Merényi et al. 1994; for arylperoxyl radicals, see Alfassi et al. 1995]. The highly chlorinated peroxyl radicals oxidize some nucleobase anions (at high pH) quite effectively (Kapoor and Gopinathan 1992), but their reduction potential is too low to oxidize even Gua at substantial rates in neutral solutions.

A similar gradation is observed, when $O_2^{\bullet-}$ is the reductant. The rate of the reaction of the most powerful peroxyl radical, the acetylperoxyl radical, with $O_2^{\bullet-}$ is close to diffusion-controlled [reaction (7); $k \approx 10^9$ dm^3 mol^{-1} s^{-1}; Schuchmann and von Sonntag 1988], while the α-hydroxyethylperoxyl radical reacts with $O_2^{\bullet-}$ merely with a rate constant near 10^7 dm^3 mol^{-1} s^{-1} (Bothe et al. 1983).

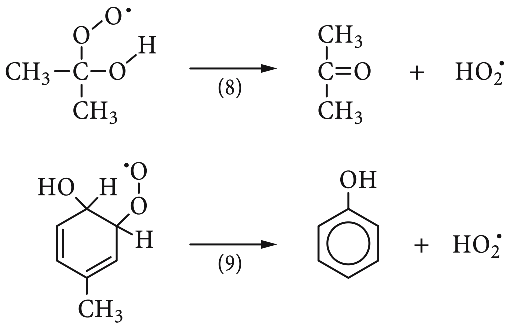
$$CH_3C(O)OO^{\bullet} + O_2^{\bullet-} \rightarrow CH_3C(O)OO^- + O_2 \qquad (7)$$

The peroxyl radical group is among the most strongly electron-withdrawing substituents (Schuchmann et al. 1989), and in a plot of the pK_a values of substituted acetic acids vs. the Taft σ* constant its value of 3.7 falls in between those of the cyano and nitro groups. This strong electron withdrawing property of the peroxyl radical function strongly lowers, of course, the pK_a value of the peroxyl radical compared to that of the parent compound (acetic acid: Schuchmann et al. 1989; malonic acid: Schuchmann et al. 2000; formamide: Muñoz et al. 2000). pK_a values of peroxyl radicals can be predicted (Muñoz et al. 2000) using the above Taft σ* value and the compiled Taft parameters (Perrin et al. 1981).

8.4

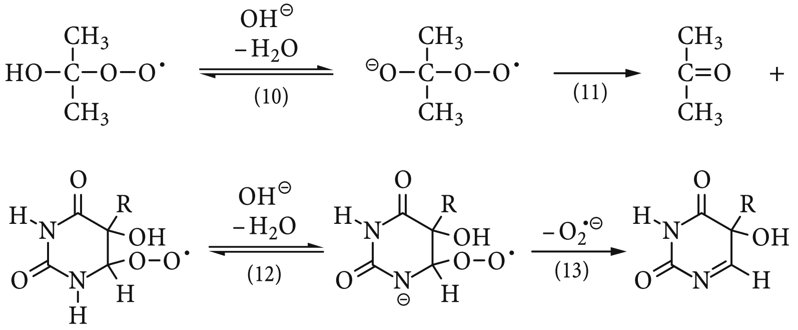
$HO_2^{\bullet}/O_2^{\bullet-}$-Elimination Reactions

Peroxyl radicals undergo a number of unimolecular processes. The most ubiquitous one is the elimination of $HO_2^{\bullet}/O_2^{\bullet-}$. They govern the peroxyl free-radical chemistry of carbohydrates (von Sonntag 1980) and prevent their autoxidation in aqueous solution (Schuchmann and von Sonntag 1978). The driving force of the $HO_2^{\bullet}$ elimination is due to the formation of a double bond [e.g., reactions (8) and (9); $k_8 = 650$ s^{-1}; $k_9 = 800$ s^{-1}; Bothe et al. 1977, 1983; Pan and von Sonntag 1990; Wang et al. 1993; Pan et al. 1993; Fang et al. 1995a]. It has been suggested that this reaction occurs via a five-membered transition state (Bothe et al. 1977), and largely due to steric reasons only the 1,2- but not the 1,4-hydroxycyclohexadienylperoxyl radical eliminates $HO_2^{\bullet}$ (Pan et al. 1993).



The rate of $HO_2^{\bullet}$ elimination from α-hydroxyalkylperoxyl radicals strongly depends on the flanking substituents that also govern the strength of the resulting C-O double bond (for a compilation see von Sonntag and Schuchmann 1997).

The $O_2^{\bullet-}$-elimination reactions may be divided into three groups. Those peroxyl radicals that have an –OH or –NH function in the α-position make up the first group. Such peroxyl radicals play a major role in nucleobase peroxyl radical chemistry [cf. reactions (12) and (13)]. Upon deprotonation at the heteroatom by OH^- [reactions (10) and (12)], the peroxyl radical anion is formed (cf. the enhancement of the acidity of the functions α to the peroxyl group discussed above; for the thermodynamics of the various equilibria that are involved in these reactions see Goldstein et al. 2002). As before, the driving force for the elimination reaction is the formation of a double bond [in addition to the energy gain by the formation of the stabilized $O_2^{\bullet-}$ radical [cf. reactions (11) and (13)].



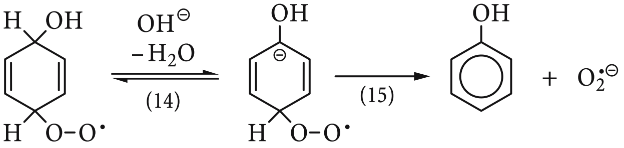
The peroxyl radical anion formed in reaction (10) has an immeasurably short (<< 10^{-6} s^{-1}) lifetime, i.e., k_{11} is much larger than $k_{-10} \times [H_2O]$, and even at high $[OH^-]$ the rate of acetone formation is essentially given by $k_{10} \times [OH^-]$ (Bothe et al. 1977). The situation is similar for other α-hydroxyalkylperoxyl radical anions (Rabani et al. 1974; Ilan et al. 1976; Bothe et al. 1983) with the exception

Table 8.1. pK_a values of radical derived from glycine and alanine anhydrides. Rates of $O_2^{\bullet -}$-elimination of their peroxyl radical anions. (Mieden and von Sonntag 1989; Mieden et al. 1993)

Parameter	Glycine anhydride	Alanine anhydride
pK_a of parent radical	9.8	10.6
pK_a of peroxyl radical	10.7	11.2
$k(O_2^{\bullet -}$ elimination) s^{-1}	1.6×10^5	3.9×10^6

of the peroxyl radical derived from hydroxymalonic acid, where the $O_2^{\bullet -}$-elimination from the peroxyl radical anion is not much faster than the $HO_2^{\bullet}$ elimination of from the protonated form (Schuchmann et al. 1995). Also relatively long lifetimes with respect to $O_2^{\bullet -}$-elimination are given by the peroxyl radical anions derived from uracil (Schuchmann and von Sonntag 1983; Schuchmann et al. 1984), atrazine (Tauber and von Sonntag 2000), formamide (Muñoz et al. 2000) and cyclic dipeptides (Mieden et al. 1993). For the latter system more detailed data are available (Table 8.1). Substitution of the prototype radical by an electron donating methyl group raises the pK_a values. For the same reason, the rate of $O_2^{\bullet -}$-release is enhanced by methyl substitution.

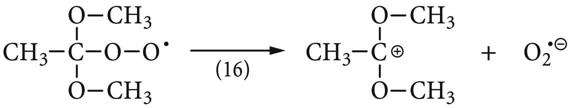
The second group is related to the first group, but here a distant *carbon*-bound hydrogen must be removed. A case in point is the 1-hydroxycyclohexadienyl-4-peroxyl radical [reactions (14) and (15)].



Whereas base-induced deprotonation at a heteroatom is very fast (practically diffusion-controlled), deprotonation at carbon is generally much slower (Eigen et al. 1964, 1965). Thus, this type of $O_2^{\bullet -}$-elimination is observed at higher pH values compared to the reactions discussed before. The elimination of $HO_2^{\bullet}$ is subject to steric restrictions,$^-$ but the OH^--induced $O_2^{\bullet -}$-elimination is not, and at high pH all hydroxycyclohexadienylperoxyl radicals eliminate $O_2^{\bullet -}$ bringing the phenolate yield close to 100% [reactions (9) and (14)/(15)]; competing reactions (see below) are thereby suppressed.

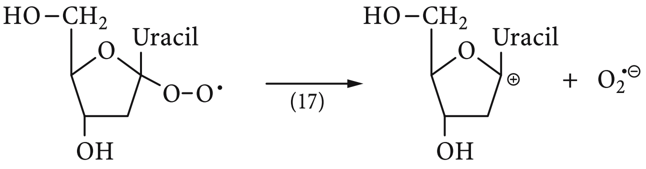
Experiments are often and carried out in the presence of buffer. Thus, it is important to note that the $O_2^{\bullet -}$-elimination of α-hydroxyalkylperoxyl radicals is not only induced by OH^- but also by buffer, albeit with a much lower rate constant [1-hydroxyethylperoxyl radical: $k(OH^-) = 4 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$; $k(HPO_4^{2-}) = 4 \times 10^6\ dm^3\ mol^1\ s^{-1}$; Bothe et al. 1983].

The third class of peroxyl radicals is characterized by a dissociation into a carbocation and $O_2^{\bullet -}$. One example has been unequivocally established to date [reaction (16); $k = 6.5 \times 10^4\ s^{-1}$; Schuchmann et al. 1990].



$$CH_3-\overset{\overset{\displaystyle O-CH_3}{|}}{\underset{\underset{\displaystyle O-CH_3}{|}}{C}}-O-O^{\bullet} \xrightarrow[(16)]{} CH_3-\overset{\overset{\displaystyle O-CH_3}{|}}{\underset{\underset{\displaystyle O-CH_3}{|}}{C}}{}^{\oplus} + O_2^{\bullet\ominus}$$

Here, the driving force is provided by the stabilization of the cation by the adjacent electron-donating groups. It is typical for ionic dissociation processes that the rates depend strongly on the stabilization energies of the ions formed, and it is hence not surprising that the peroxyl radicals derived from diisopropylether (Schuchmann and von Sonntag 1987) and 1,3-dioxane (Nese et al. 1995) do not display a similarly fast $O_2^{\bullet -}$-elimination, as the former lacks the second alkoxyl function and the latter the methyl substituent. It has been suggested that also in the case of the *C*(1′) nucleoside radicals (formed through the photolysis of the pivaloyl derivative) this reaction plays a role [reaction (17); Emanuel et al. 1999]. However, the observation that the radicals generated in the photolysis of di-*tert*-butylketone undergo the same reactions has to be taken as a caveat.



In reactions (18) and (19) (Das et al. 1987), no peroxyl radical intermediates have been observed, but if they existed, they would compound among this group.

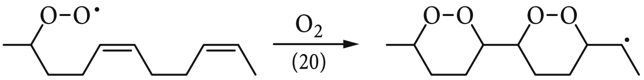
$$CO_2^{\bullet -} + O_2 \rightarrow CO_2 + O_2^{\bullet -} \tag{18}$$

$$^{\bullet}CH_2N(CH_3)_2 + O_2 \rightarrow (CH_3)_2N{=}CH_2^{+} + O_2^{\bullet -} \tag{19}$$

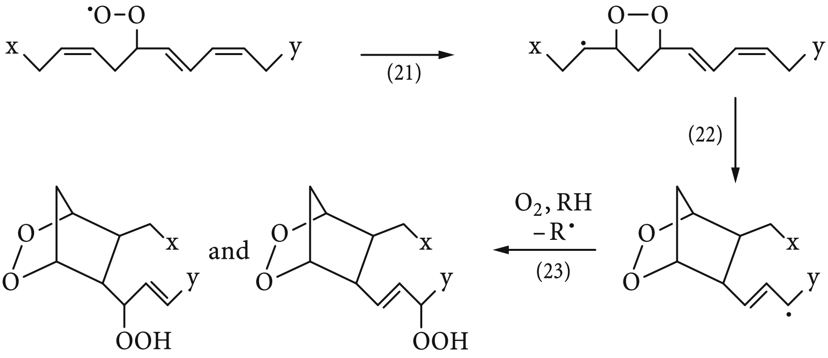
The rate constant of reaction (18) is close to diffusion controlled, and values ranging between $2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (Adams and Willson 1969; Buxton et al. 1976) and $4.2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (Ilan and Rabani 1976) have been reported.

8.5
Addition to the C–C Double Bond

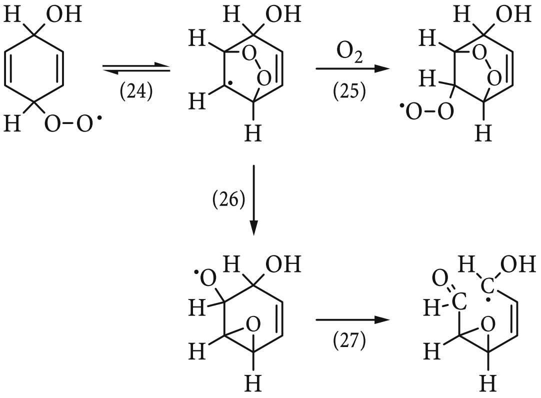
The addition of peroxyl radicals to double bonds is generally not very fast, and even with β-carotene the rate constant is less than $10^6\ dm^3\ mol^{-1}\ s^{-1}$ (Mortensen and Skibsted 1998). Nevertheless, peroxyl radicals of multi-unsaturated compounds have been reported to undergo chain-like peroxidation if the C-C double bonds are suitably disposed [cf. reaction (20); Porter et al. 1980, 1981].



The autoxidation of polyunsaturated fatty acids (cf. Porter et al. 1981) is usually monitored by the formation of “malonaldehyde” using the 2-thiobarbituric acid essay. This is carried out under rather severe conditions which decomposes its precursor. This malonaldehyde-like product is obviously formed via a cyclization reaction of a peroxyl radical, followed by other processes such as further cyclization and hydroperoxide formation [reactions (21)–(23)]. The resulting hydroperoxides may eliminate malonaldehyde upon a homolytic cleavage of the endoperoxidic intermediate (Pryor and Stanley 1975).

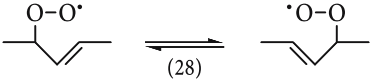


In the series of hydroxycyclohexadienylperoxyl radicals, one encounters the competition between the $HO_2^\bullet/O_2^{\bullet-}$ elimination leading to phenol [reactions (9) and (14)/(15)] and fragmentation of the ring (Pan et al. 1993). That latter has been attributed to an intramolecular addition of the peroxyl radical function to a diene double bond [reaction (24)]. This reaction is reversible [reaction (-24)], but when O_2 adds to the newly created carbon-centered radical the endoperoxidic function is locked in [reaction (25)]. In analogy to reaction (24), the first step of the trichloromethylperoxyl-radical-induced oxidation of indole is its addition to the indole *C*(2)-*C*(3) double bond (Shen et al. 1989).



In competition with O_2-addition [reaction (25)], the β-alkylperoxide species may undergo radical-induced cleavage of the peroxide function [reaction (26); Bloodworth et al. 1984; Phulkar et al. 1990].

In allylperoxyl radicals, allylic rearrangement leads to the 1,3-migration of the peroxyl function, with the corresponding shift of the double bond [reaction (28); Schenck et al. 1958].

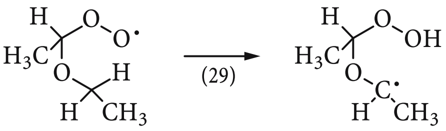


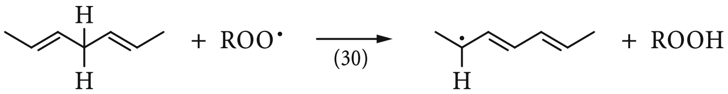
Evidence has been adduced that for many such systems, the apparently obvious cyclic intermediate 1,2-dioxanyl is not realized in the course of this rearrangement: an O_2–allylradical pair is postulated instead (Beckwith et al. 1989; Porter et al. 1994). Nevertheless, this cyclic structure has been invoked in the gas phase (Lodhi and Walker 1991; Bozzelli and Dean 1993), and an exothermicity of 96 kJ mol^{-1} has been computed for the formation of the cyclic intermediate relative to the level of allyl plus O_2 (Bozzelli and Dean 1993).

In DNA free-radical chemistry allylperoxyl radicals play a major role in the free-radical-induced oxidation of Thy. Thus far, this kind of rearrangement has not yet been observed (but also not especially looked for) in this system.

8.6
Intramolecular and Intermolecular H-Abstraction Reactions

The H-abstraction reactions of peroxyl radicals are related to ET discussed above, as in both cases the same final product is formed, a hydroperoxide. Mechanistically, these two processes are, of course, different. Hydrogen-abstraction reactions by peroxyl radical, including $HO_2^•$, are common (cf. the autoxidation of polyunsaturated lipids;Hasegawa and Patterson 1978; Patterson and Hasegawa 1978; Patterson 1981; Porter et al. 1981; Gebicki and Bielski 1981; Barclay et al. 1989; Zhu and Sevilla 1990; Aikens and Dix 1991; Simic et al. 1992). This H-abstraction reaction may occur *intra*molecularly as well as *inter*molecularly [cf. reactions (29) and (30)].





The ROO-H BDE in hydroperoxides derived from weakly oxidizing peroxyl radicals is ca. 360-370 kJ mol^{-1} (Khursan and Martem'yanov 1991; Denisov and Denisova 1993), and, for a peroxyl radical reaction to occur at an appreciable rate, the C-H BDE of the donor must be sufficiently low. A case in point is aliphatic amines, but even with these the rate constants are rather low ($k < 500\ dm^3\ mol^{-1}\ s^{-1}$ at 350 K; Dambrova et al. 2000). In DNA, the weakest C-H bond is that of the allylic hydrogen in Thy, and this is the preferred site of peroxyl radical attack (Razskazovskii and Sevilla 1996; Martini and Termini 1997). In poly(U), nucleobase peroxyl radicals abstract the $C(2')$-H that is activated by the neighboring OH group (Chaps 9.4 and 11.2), but $C(2')$-H abstraction in DNA is inefficient due to the higher BDE of this hydrogen.

Because of the often slow rate of reaction, even of intramolecular H-abstraction and a favorable six-membered transition state such as in reaction (29) ($k \approx 1\ s^{-1}$; Schuchmann and von Sonntag 1982; for further examples see, e.g., Ulanski et al. 1996a,b), the reaction is only observed at a low steady-state of peroxyl radicals, that is, when the lifetime of peroxyl radical is long. Kinetic parameters with pre-exponential factors near 10^8 and activation energies varying from 30-60 kJ mol^{-1} have been reported for the reactions of peroxyl radicals with various alcohols (Denisov and Denisova 1993).

As a consequence of the reformation of the starting radical, a chain sets in [reactions (31)-(33)].

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \tag{31}$$

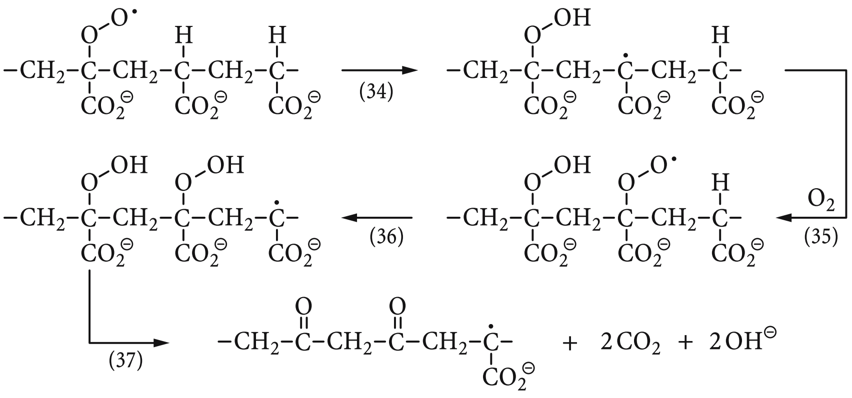
$$RO_2^{\bullet} + RH \rightarrow RO_2H + R^{\bullet} \tag{32}$$

$$2\ RO_2^{\bullet} \rightarrow \text{Products} \tag{33}$$

If this mechanism is strictly followed the chain length and hence the value of O_2-uptake (see below) increases linearly with the substrate concentration and (initiation rate)$^{-1/2}$ (i.e., in radiolytic studies the dose rate) and in charged polymers also on the pH (cf. Ulanski et al. 1996a). In polymers, the chain reaction may mainly proceed intramolecularly (Ulanski et al. 1996a; Janik et al. 2000). An example for an efficient intramolecular autoxidation is poly(acrylic acid) [reactions (34)–(36); Ulanski et al. 1996a]. In these autoxidation reactions, hydroperoxides are formed which, in some cases, are quite unstable [e.g. reaction (37); see also Leitzke et al. 2001].

In micellar systems, the chain peroxidation reaction only becomes effective at the critical micelle concentration where the substrate molecules aggregate thereby forming locally high concentrations (Gebicki and Allen 1969).

The hydroperoxides that are formed in all these autoxidation reactions all have low O-H BDEs. As a consequence, hydroperoxides are good H-donors in *non-aqueous* media, and they are often used to intercept radicals by H-donation. However, in water, where this function is hydrogen-bonded, the H-abstraction rates can drop by several orders of magnitude; the same phenomenon is observed with phenols (Das et al. 1981; Avila et al. 1995; Valgimigli et al. 1995; Banks et al. 1996; see also Ulanski et al. 1999).



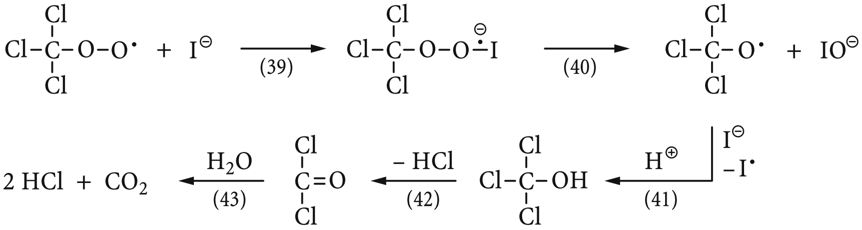
8.7
O-Transfer Reactions

O-transfer reactions of peroxyl radicals are sometimes referred to as two-electron reductions (Bonifacic et al. 1991; Schöneich et al. 1991; Merényi et al. 1994), in analogy to the one-electron reduction discussed above, although the reaction type is quite different. It requires the addition of the peroxyl radical to an electron-rich center and is thus reminiscent of the O-transfer in ozone reactions (Muñoz and von Sonntag 2000; Muñoz et al. 2001; Flyunt et al. 2003). In some cases, this complex may simply decay into an oxyl radical and an oxide as observed with diaryltellurides (Engman et al. 1995), phosphines (Engman et al. 1995) and disulfides [Schöneich et al. 1991; Bonifacic and Stefanic 2000; e.g., reaction (38)].

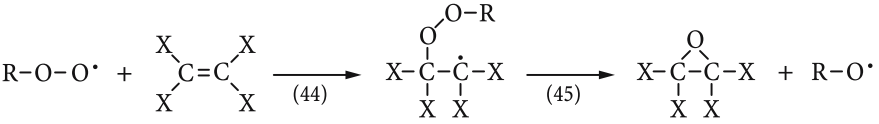
$$\text{R-O-O}^\bullet + (\text{CH}_3)_2\text{S} \rightarrow \text{R-O}^\bullet + (\text{CH}_3)_2\text{S=O} \qquad (38)$$

In the case of tellurides, strongly oxidizing peroxyl radicals may also undergo ET in competition, and the adduct to phosphines may be sufficiently long-lived to react further with O_2 (Engman et al. 1995).

The trichloromethylperoxyl radical adds to the iodide ion [reaction (39)] with subsequent decomposition into the trichloromethoxyl radical [reaction (40)] which is further reduced by iodide into trichloromethanol [reaction (41); Bonifacic et al. 1991]. Its decay is much faster [reaction (42), $k \geq 8 \times 10^4$ s^{-1}] than the subsequent hydrolysis of phosgene [reaction (43), $k = 9$ s^{-1} at 25 °C, $E_a = 53$ kJ mol^{-1}; Mertens et al. 1994].



The reaction of peroxyl radicals with alkenes may give rise to epoxides [reactions (44) and (45); cf.; Morgan et al. 1984; Sawaki and Ogata 1984].



The rate constant increases with increasing electron-donating capacity of the C-C double bond (Shoute et al. 1994) and oxidative power of the peroxyl radical (Sawaki and Ogata 1984), and the addition of acylperoxyl radicals has been found to be about 10^5 times faster than that of alkylperoxyl radicals. In the gas phase, the propyl-2-peroxyl radical adds to 2,3-dimethylbut-2-ene with a rate constant of $\approx 6\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ (Sway and Waddington 1982). With rate constants as low as this, the addition reaction (44) must be the rate determining step of epoxide formation, since the rate of the subsequent step (45) ranges from $10^2\ \mathrm{s^{-1}}$ (Phulkar et al. 1990) to $10^6\ \mathrm{s^{-1}}$ (Bloodworth et al. 1984).

8.8
Bimolecular Decay of Peroxyl Radicals

Peroxyl radicals which do not decay by one of the unimolecular processes discussed above must disappear bimolecularly. In contrast to many other radicals, they cannot undergo disproportionation. Hence they are left to decay via the recombination process, the results of which is a tetroxide intermediate [reaction (46); an exception may be their reaction with $O_2^{\bullet -}$; cf. reaction (7)].,

$$2\,\mathrm{ROO^{\bullet}} \rightleftharpoons \mathrm{R{-}O_4{-}R} \qquad (46)$$

The tetroxide intermediate is a well-established in organic solvents at low temperatures (Bartlett and Guaraldi 1967; Adamic et al. 1969; Bennett et al. 1970; Howard and Bennett 1972; Howard 1978; Furimsky et al. 1980). However at the temperatures accessible in aqueous solutions the tetroxide, owing to its low ROO-OOR BDE, estimated at 21-33 kJ $\mathrm{mol^{-1}}$ (Benson and Shaw 1970; Nangia and Benson 1979; Bennett et al. 1987; Francisco and Williams 1988), can only attain a very low steady-state concentration. Even at the high radical concentrations achievable in the pulse radiolysis experiment, it has not yet been detected. Various decay processes of the tetroxide limits its steady-state concentration: the reverse reaction [reaction (-46)] and its decay into products [reactions (47)–(50), R = alkyl or H]. Most primary (and also some secondary) peroxyl radical decay with rate constants around $10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ (Neta et al. 1990).

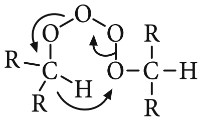
$$\mathrm{R_2CH{-}O_4{-}CHR_2 \rightarrow R_2C{=}O + R_2CHOH + O_2} \qquad (47)$$

$$\mathrm{R_2CH{-}O_4{-}CHR_2 \rightarrow 2\,R_2C{=}O + H_2O_2} \qquad (48)$$

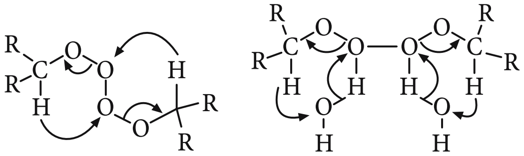
$$R_2CH\text{-}O_4\text{-}CHR_2 \rightarrow 2\,R_2CHO^{\bullet} + O_2 \qquad (49)$$

$$R_2CH\text{-}O_4\text{-}CHR_2 \rightarrow R_2CHOOCHR_2 + O_2 \qquad (50)$$

Depending on the identity of the peroxyl radicals involved, reactions (47)-(50) may occur in differing proportions. In particular, the product-forming self reaction of tertiary peroxyl radicals is restricted to path (49) and (50), since path (47) and (48) require the existence of C-H α to the peroxyl function. The exact mechanism of these reactions is still controversial, that is, whether the product-forming processes are sequential or concerted. Reaction (47) has been described by Russell (1957) as a concerted process, and this process bears his name. It is formulated as having a six-membered transition state.



Concerted decay
"Russell mechanism"



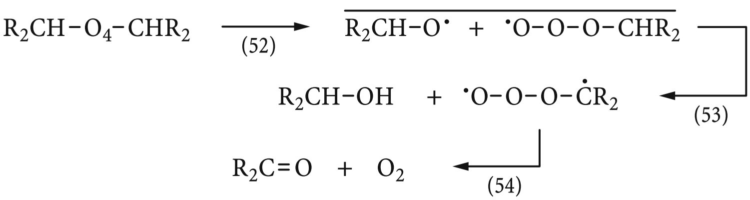
Concerted decay, without and with two water molecules
"Bennett mechanism"

Starting from a singlet ground state, the tetroxide gives rise to the carbonyl compound, a hydroxyl compound (usually an alcohol), and O_2, perhaps as singlet dioxygen ($O_2{}^1\Delta_g$) (Nakano et al. 1976; Niu and Mendenhall 1992). Alternatively, O_2 can be formed in its triplet ground state, and the carbonyl compound in its triplet excited state, which is the cause of the chemiluminescence observed in these reactions (Lee and Mendenhall 1988; Mendenhall et al. 1991; Vasvary and Gal 1993).

The concertedness of reaction (47) has been questioned on energetic and several other grounds (Nangia and Benson 1980; Khursan et al. 1990). It has been proposed instead that the carbonyl oxide ($RCH{=}O^+\text{-}O^-$; the Criegee intermediate), and the alkoxyl radical $R_2CHO^{\bullet}$ play a central role. For aqueous media, this hypothesis which implies a chain reaction (Nangia and Benson 1980) must be ruled out, since on account of the rapid 1,2-H-shift of primary and secondary oxyl radicals under these conditions [reaction (51); Berdnikov et al. 1972; Gilbert et al. 1976, 1977; Schuchmann and von Sonntag 1981] they cannot fulfill their function as chain carrier. Moreover, in the case of the methylperoxyl radical, it could be shown that in aqueous solution the corresponding carbonyloxide may at best play a minor role (Schuchmann and von Sonntag 1984).

$$R_2CH\text{-}O^{\bullet} \rightarrow {}^{\bullet}CR_2OH \qquad (51)$$

Asymmetric O-O bond homolysis of the tetroxide as a first step to product formation has been invoked (Khursan et al. 1990), and the idea of the Russell mechanism replaced by a three-step mechanism [reactions (52)–(54)].



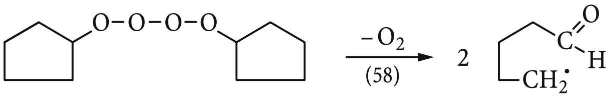
Process (48), sometimes termed Bennett mechanism, yields H_2O_2 and two carbonyl compounds. It has often been thought of as being concerted, proceeding via two five-membered rings (Bennett and Summers 1974; Bothe and Schulte-Frohlinde 1978) or two six-membered rings involving two water molecules (see above). This has been criticized on account of the excessive entropic requirements of the bicyclic transition state, and, following the lateral cleavage (55), reactions (56) and (57) have been proposed instead (Khursan et al. 1990; for a discussion, see von Sonntag and Schuchmann 1997).

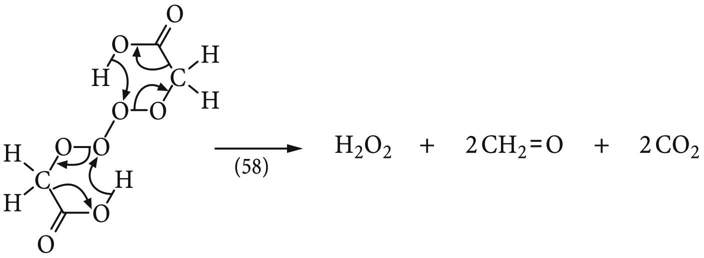
$$R_2CHO^\bullet + {}^\bullet OOOCHR_2 \rightarrow R_2C{=}O + HOOOCHR_2 \qquad (55)$$

$$HOOOCHR_2 \rightarrow HO_2^\bullet + {}^\bullet OCHR_2 \qquad (56)$$

$$HO_2^\bullet + {}^\bullet OCHR_2 \rightarrow H_2O_2 + O{=}CHR_2 \qquad (57)$$

As far as concerted reactions are concerned, it should be mentioned that two other processes of considerable concertedness have been recognized in the studies of the fate of the peroxyl radicals derived from cyclopentane and cyclohexane [e.g., reaction (58); Zegota et al. 1984] and acetate [reaction (59); Schuchmann et al. 1985].





8.9
Alkoxyl Radicals in Peroxyl Radical Systems

In most peroxyl radical systems investigated so-far alkoxyl radicals play a certain, albeit often not dominating role [cf. reaction (49)]. As mentioned above and discussed in more detail in Chap. 7.2, primary and secondary alkoxyl radicals undergo in water rapid ($k \approx 10^6\ \mathrm{s}^{-1}$) 1,2-H-shift [reaction (51)]. In competition, β-fragmentation also occurs [reaction (60)].

$$R_3C\text{-}O^\bullet \rightarrow R^\bullet + R_2C{=}O \qquad (60)$$

The rate of this reaction (which is the main decay of tertiary alkoxyl radicals) is also strongly enhanced in water as compared to the gas phase and organic solvents. If different substituents can be cleaved off, it is the more highly-substituted one (weaker C-C bond) that is broken preferentially (Rüchardt 1987). Thus in the case of secondary alkoxyl radicals, substitution in β-position also decides the ratio of 1,2-H-shift and β-fragmentation (Schuchmann and von Sonntag 1982). Because of the fast 1,2-H-shift and β-fragmentation reactions in water, intermolecular H-abstraction reactions of alkoxyl radicals [reaction (61)] are usually inefficient, but intramolecular H-abstraction may occur quite readily if an H atom is in a favorable distance (e.g., six-membered transition state).

$$R_3CO^\bullet + RH \rightarrow R_3COH + R^\bullet \qquad (61)$$

Because of the rapid 1,2-H-shift [reaction (51)] and the ready conversion of the ensuing α-hydroxyalkyl radical into $HO_2^\bullet/O_2^{\bullet-}$ by O_2 [cf. reactions (8) and (10)/(11)], primary and secondary peroxyl are often the precursor of $O_2^{\bullet-}$ in these systems. Furthermore, the β-fragmentation reaction (60) creates a new radical and hence a new peroxyl radical, a situation which makes the elucidation of mechanistic details often very difficult if not impossible. The peroxyl radical systems that have been investigated in detail thus far have been discussed by von Sonntag and Schuchmann (1997).

8.10
Oxygen Uptake

Oxygen uptake measurements can give considerable mechanistic information. In normal peroxyl radical reactions the $G(O_2\text{-uptake})$ will range between 3×10^{-7} and $6 \times 10^{-7}\ \mathrm{mol\ J^{-1}}$ (Table 8.2). The lower value will be found when half of the O_2 is reformed (for example, the formate system), the higher value when all O_2 is consumed during the decay of the peroxyl radicals. As soon as $G(O_2\text{-uptake})$ exceeds the upper limit of $6 \times 10^{-7}\ \mathrm{mol\ J^{-1}}$, a chain reaction must prevail [examples are some polymers including poly(U)]. However, there is also the interesting situation that $G(O_2\text{-uptake})$ is below $3 \times 10^{-7}\ \mathrm{mol\ J^{-1}}$. This means that some of the radicals do not react with O_2. A case in point are the $^\bullet OH$-induced reactions of purines (Chap. 10.3).

Table 8.2. *G* values (unit: 10^{-7} mol J^{-1}) of O_2-uptake in the γ-radiolysis of several substrates in N_2O/O_2-saturated solutions. For substrate concentrations and dose rates see the original literature

Substrate	$^•OH$	Tl(II)	Reference
Formate	3.1 3.1		Isildar et al. (1982) Al-Sheikhly (1994)
2-PrOH	3.1		Isildar et al. (1982)
*t*BuOH	4.5		Isildar et al. (1982)
Diethyl ether	4.7		Isildar et al. (1982)
Carbowax 20 M	10.6		Isildar et al. (1982)
Poly(acrylic acid), pH 10	100		Ulanski et al. (1996a)
Poly(methyl vinyl ether)	110		Janik et al. (2000)
2-Deoxyribose	3.1 3.1	 0.77	Isildar et al. (1982) Al-Sheikhly (1994)
Thy	4.2		Isildar et al. (1982)
Cyt	4.6		Isildar et al. (1982)
Ura	5.2		Isildar et al. (1982)
Thd	5.0		Isildar et al. (1982)
dAdo	1.4 1.75	0.72	Isildar et al. (1982) Al-Sheikhly (1994)
Ade	2.7	0.82	Al-Sheikhly (1994)
dGuo	1.6		Isildar et al. (1982)
dGuo	1.5	0.72	Al-Sheikhly (1994)
Guo	1.5	0.72	Al-Sheikhly (1994)
TMP	4.6		Isildar et al. (1982)
dCMP	5.0		Isildar et al. (1982)
dAMP	2.0		Isildar et al. (1982)
dGMP	1.7		Isildar et al. (1982)
UMP	6.6		Isildar et al. (1982)
poly(U)	21.8		Isildar et al. (1982)
poly(A)	3.6		Isildar et al. (1982)
ssRNA	4.2		Isildar et al. (1982)
ssDNA	7.1		Isildar et al. (1982)
Mixture of 2′-deoxynucleotides as in DNA	3.3		Isildar et al. (1982)
Ditto calculated from the above data	3.3		Isildar et al. (1982)

8.11
The Superoxide Radical

In the preceding paragraphs, various routes to $HO_2^{\bullet}/O_2^{\bullet -}$ upon unimolecular and bimolecular decay of peroxyl radicals have been shown. Although these reactions will certainly contribute, in a living cell the main source of $O_2^{\bullet -}$ is a side reaction in the energy-providing mitochondrial metabolism (Turrens 1997; for an estimate of cellular steady-state concentrations see Boveris and Cadenas 1997). In a human, its production has been estimated at 0.2-0.4 mol/day. Especially, when cells residing in a hypoxic condition are exposed to O_2, large quantities of $O_2^{\bullet -}$ are set free, an effect that contributes to, if it is not the cause of, ischemia. Moreover, $O_2^{\bullet -}$ is produced in large quantities by macrophages as a part of their defense system. Thus, $O_2^{\bullet -}$ is the most ubiquitous peroxyl radical. In a cellular environment it must exert severe damage (Fridovich 1978), and it is generally considered to be a major player in what is termed as "oxidative stress" (Sies 1986, 1991; for the repair of oxidative damage in mitochondrial DNA see Bohr 2002). Evolution produced enzymes, the superoxide dismutases (SOD), to keep cellular $O_2^{\bullet -}$ steady-state concentration low (for reviews see Fridovich 1975; Oberley 1982).

There are three types of SOD. All SODs have transition metal ions in their reaction center, and the enzymes in both high and low oxidation states react readily ($k \approx 2 \times 10^9$ dm^3 mol^{-1} s^{-1}; Klug et al. 1972; Fielden et al. 1974; Pick et al. 1974) with $O_2^{\bullet -}$ [written with Cu as an example; reactions (62) and (63)] which allows the enzyme to be recycled.

$$\mathrm{SOD(Cu^{2+})} + O_2^{\bullet -} \rightarrow \mathrm{SOD(Cu^{+})} + O_2 \qquad (62)$$

$$\mathrm{SOD(Cu^{+})} + O_2^{\bullet -} + 2\,H^{+} \rightarrow \mathrm{SOD(Cu^{2+})} + H_2O_2 \qquad (63)$$

The one isolated from bovine blood contains Cu in its reaction center as well as Zn which appears not to take part in the dismutation process. The other two types of SOD contain either Fe or Mn. The CuZn SOD has been found only in eukariotic cells, the Fe SOD only in prokaryotic cells, and the Mn SOD in both (Fee 1981). Aqua-Mn^{2+} cannot be reduced by $O_2^{\bullet -}$, but is forms a complex that dismutates giving rise to H_2O_2 and O_2 (Jacobsen et al. 1997). Such intermediates may also play a role in Mn SOD.

For the study of its reaction in aqueous solutions, $O_2^{\bullet -}/HO_2^{\bullet}$ may be generated by various means (for a review see Cabelli 1997). One possibility is the vacuum-UV photolysis of aqueous solutions of EtOH at high pH (Bielski and Gebicki 1982; for a review on VUV photolysis of alcohols, see von Sonntag and Schuchmann 1977). Under these conditions, α-hydroxyalkyl is generated which, as discussed above, is readily converted by O_2 to $O_2^{\bullet -}$, which is long-lived at high pH (see below). This method of generating $O_2^{\bullet -}$ has the advantage that besides EtOH and some acetaldehyde no further potentially reactive material is present in these $O_2^{\bullet -}$ solutions. For the photolytic generation of $O_2^{\bullet -}$ at longer wavelengths, the reaction of n→π* excited benzophenone with alcohols in aqueous solution can be used as well (McDowell et al. 1983). Alternatively, it also can be generated radiolytically in O_2-containing aqueous formate solution (Bielski and Richter 1977). Dissolving KO_2 in DMSO also affords $O_2^{\bullet -}$, and in a stopped-flow system this solution may be diluted with water, allowing the study of $O_2^{\bullet -}$ at least at a moderately alkaline pH (Bull et al. 1983). The thermal decomposition of the azo compound di(4-caboxybenzoyl)hyponitrite (SOTS-1) also yields $O_2^{\bullet -}$ (Ingold et al. 1997; Chap. 2.4). Most commonly, $O_2^{\bullet -}$ is generated enzymatically by xanthine/xanthine oxidase. Thereby, the reduced xanthine oxidase reacts with O_2 to produce $O_2^{\bullet -}$ via a stepwise mechanism (Fridovich 1970), and altogether two $O_2^{\bullet -}$ radicals are generated for each xanthine oxidized. A caveat has been expressed (Ingold et al. 1997) that the enzyme may contain an excess of transition metal ions which can lead to the formation of $^{\bullet}OH$ via the Fenton reaction, which then can suggest a reactivity of $O_2^{\bullet -}$, which in fact does not exist. The fact that $O_2^{\bullet -}$ is formed in some autoxidation reactions has been connected with the cytotoxic properties of such compounds (Cohen and Heikkila 1974).

In neutral solution, $O_2^{\bullet -}$ dominates. The $pK_a(HO_2^{\bullet}) = 4.8$ is the selected value (Bielski et al. 1985) from a series of determinations (Czapski and Bielski 1963; Czapski and Dorfman 1964; Sehested et al. 1968; Rabani and Nielsen 1969; Behar et al. 1970). The rate of self-termination of $HO_2^{\bullet}/O_2^{\bullet -}$ strongly depends on pH, since only reactions (64) and (65) proceed at an appreciable rate ($k_{64} = 8.6 \times 10^5$ dm^3 mol^{-1} s^{-1} ; $k_{65} = 1.02 \times 10^8$ dm^3 mol^{-1} s^{-1}), while the self-termination of two $O_2^{\bullet -}$ is too slow to be measurable ($k < 0.35$ dm^3 mol^{-1} s^{-1}; Bielski et al. 1985).

$$2\,HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{64}$$

$$HO_2^{\bullet} + O_2^{\bullet -} \rightarrow HO_2^{-} + O_2 \tag{65}$$

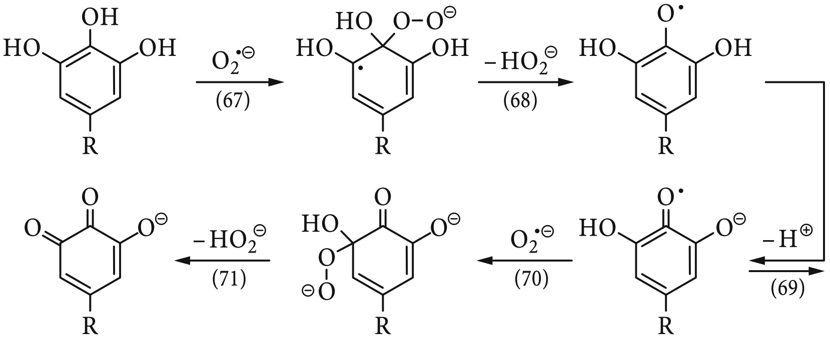
As a consequence, the observed rate of bimolecular decay has a maximum at the pK_a value, levels of at low pH at the rate constant of reaction (64), and at high pH continues to drop when $\log k_{obs}$ is plotted vs. the pH. In acid solution, the activation energy of the bimolecular decay of $HO_2^{\bullet}$ is 24 kJ mol^{-1} (Bielski and Saito 1962), in D_2O it rises to 29 kJ mol^{-1} (Bielski and Saito 1971). There is increasing evidence that little or no (<10%) singlet dioxygen ($O_2\,^1\Delta_g$) is formed upon the bimolecular decay of $HO_2^{\bullet}$ (Foote et al. 1980; Aubry et al. 1981; Arudi et al. 1984).

The detection of $O_2^{\bullet -}$ is usually based on its reducing properties ($E^7 = -0.33$ V; Ilan et al. 1974; Wardman 1989). A typical example is its reaction with TNM [reaction (66); $k = 1.9 \times 10^9$ dm^3 mol^{-1} s^{-1}; Asmus and Henglein 1964; Rabani et al. 1965] which yield the strongly absorbing nitroform anion ($\varepsilon(350\text{ nm}) = 15{,}000$ dm^3 mol^{-1} cm^{-1}].

$$O_2^{\bullet -} + C(NO_2)_4 \rightarrow O_2 + C(NO_2)_3^{-} + {}^{\bullet}NO_2 \tag{66}$$

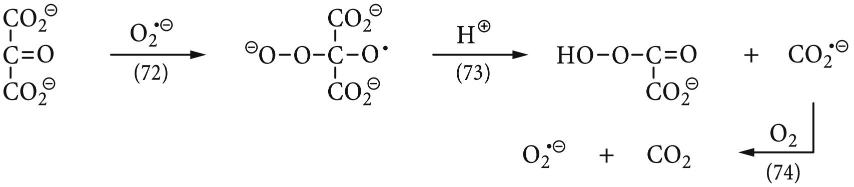
Similarly, nitro blue tetrazolium is reduced by $O_2^{\bullet -}$ ($k = 3 \times 10^4$ dm^3 mol^{-1} s^{-1}), and the mono-reduced species subsequently disproportionates yielding the two-electron-reduced monoformazan which absorbs in the visible ($\varepsilon(530) = 2.34 \times 10^3$ dm^3 mol^{-1} cm^{-1}; Bielski et al. 1980; for some of the problems that one may encounter using this assay see Cabelli 1997].

Except for ET reactions with strong oxidants, $O_2^{\bullet -}$ is not very reactive (for a compilation of rate constants, see Bielski et al. 1985). For example, practically no reaction has been detected with amino acids (Bielski and Shiue 1979), and there is no reaction to speak of with the DNA constituents, that is, it is also practically unreactive towards DNA. However, where substantial reactivity has been recognized, its main route of reaction seems to be by addition. This has not only been proposed for its reaction with pyrogallol and the propyl ester of gallic acid [$k = 3.4 \times 10^5$ and 2.6×10^5 $dm^3\ mol^{-1}\ s^{-1}$, respectively; cf. reactions (67)–(71); Deeble et al. 1987, 1988], but it seems that an addition reaction triggers a number of chain reactions (von Sonntag et al. 1993, see below).



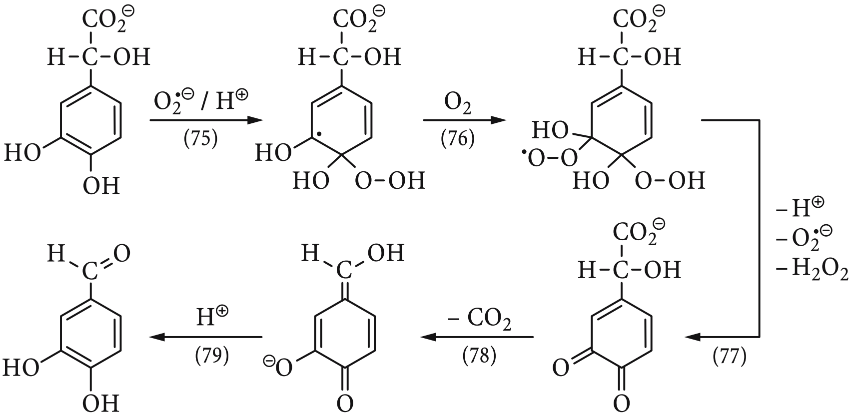
Interestingly, the reactivity of the (more oxidizing) $HO_2^{\bullet}$ radical is much less than that of $O_2^{\bullet -}$, although as a net reaction an oxidation has occurred. This has been attributed to kinetic reasons, that is, $HO_2^{\bullet}$ does not undergo addition reactions as readily as $O_2^{\bullet -}$.

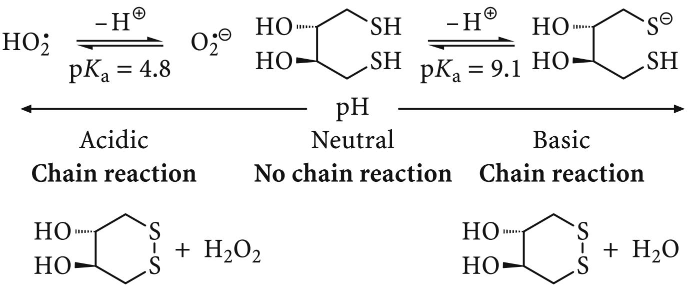
The reaction of $O_2^{\bullet -}$ with ketomalonic acid leads to oxalic peracid and CO_2 [Schuchmann et al. 1991; reactions (72)–(74)].



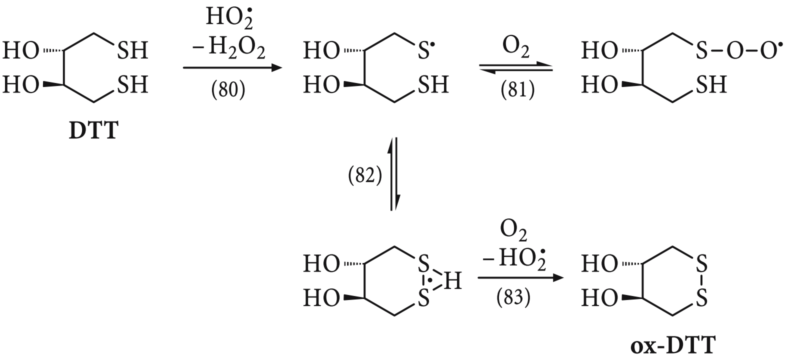
Decarboxylation is also observed in its reaction with 3,4-dihydroxymandleic acid [reactions (75)–(79); Deeble and von Sonntag 1992].

With 1,4-dithiotreitol (DTT), $O_2^{\bullet -}$ undergoes a chain reaction in basic solution. This reaction leads to 1,4-*threo*-dihydroxy-1,2-dithian (ox-DTT) and water (Zhang et al. 1991). However, when DTT is no longer deprotonated as in neutral solution, this chain reaction ceases. In acid solutions, where the $HO_2^{\bullet}$ predominates, another chain reaction takes place. It now leads to ox-DTT and H_2O_2 (Lal et al. 1997).

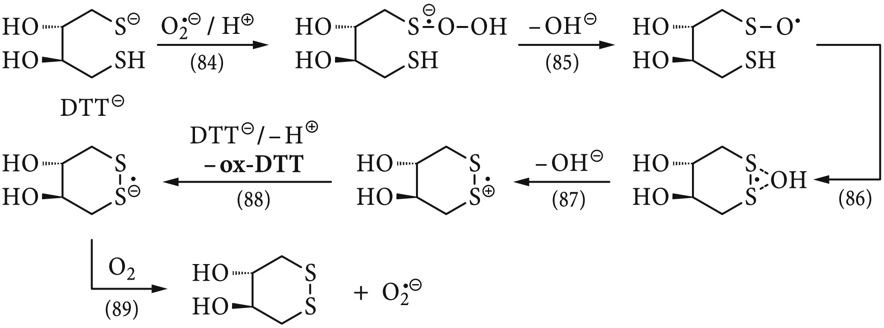




Thus, $O_2^{\bullet-}$ and $HO_2^{\bullet}$ radicals behave very differently. While the $HO_2^{\bullet}$ radical undergoes an H-abstraction [reactions (80)–(83)] and behaves like an ordinary peroxyl radical, the $O_2^{\bullet-}$ reaction sequence is initiated by an addition reaction [reaction (84), see below]. The H-abstraction reaction (80) is slow (k = 120 dm^3 mol^{-1} s^{-1}). Similar conclusions, revising an earlier report (Schulte-Frohlinde et al. 1986), have been obtained by Hildenbrand and Schulte-Frohlinde (1997) for the reaction of DNA peroxyl radicals with GSH.

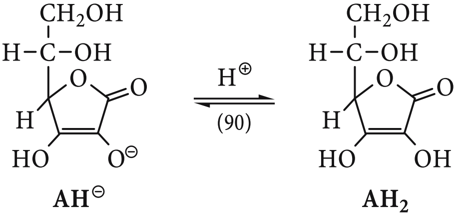


The mechanistic proposal for the chain reaction of $O_2^{\bullet-}$ with the DTT anion represented by reactions (84)–(89) (Lal et al. 1997) deviates slightly from the original proposal (Zhang et al. 1991). The essential aspect, however, remains the addition of $O_2^{\bullet-}$ to the thiolate thereby forming a three-electron-bonded intermediate [reaction (84); for other three-bonded intermediates see Chap. 7.4] and its subsequent decay into an oxidizing species [reaction (85)]. It has been calculated that the rate constant of the rate-determining step, reaction (84), is 35 dm^3 mol^{-1} s^{-1}. This reaction is even slower than the H-abstraction reaction of the $HO_2^{\bullet}$ radical discussed above.



The reactivity of a wider range of thiols toward $O_2^{\bullet-}$ has been studied (Winterbourn and Metodiewa 1999), and it has been observed that at pH 7.4 only those thiols show an appreciable reactivity who have a low pK_a value, such as penicillamine and cysteine (at pH 7, the rate constant of $O_2^{\bullet-}$ with *N*-actylcysteine is 68 dm^3 mol^{-1} s^{-1}; Benrahmoune et al. 2000). This can be rationalized by assuming that a reasonable thiolate steady-state concentration is required for the reaction to proceed. In the case of GSH the disulfide was again the major product, but the formation of some glutathionesulfonic acid was also reported (Winterbourn and Metodiewa 1994). In the biological context, the reactivity of $O_2^{\bullet-}$ with GSH is of major importance. Various rate constants are reported in the literature; the most recent re-evaluation gives now a value of ~200 dm^3 mol^{-1} s^{-1}, indicating that in a cellular environment this reaction is too slow to compete with the elimination of $O_2^{\bullet-}$ by SOD (Jones et al. 2002, 2003).

In the cellular environment, ascorbic acid (AH_2) plays a major role. Its pK_a value is at 4.3 [equilibrium (90)], and hence the ascorbate anion (AH^-) predominates around neutrality.



Both $HO_2^{\bullet}$ and $O_2^{\bullet-}$ react with ascorbate [reactions (91)–(94); Nishikimi 1975; Cabelli and Bielski 1983].

$$AH_2 + HO_2^{\bullet} \rightarrow A^{\bullet-} + H_2O_2 + H^+ \tag{91}$$

$$AH_2 + O_2^{\bullet-} \rightarrow A^{\bullet-} + H_2O_2 \tag{92}$$

$$AH^- + HO_2^{\bullet} \rightarrow A^{\bullet-} + H_2O_2 \tag{93}$$

$$AH^- + O_2^{\bullet-} \rightarrow \text{product(s)} \tag{94}$$

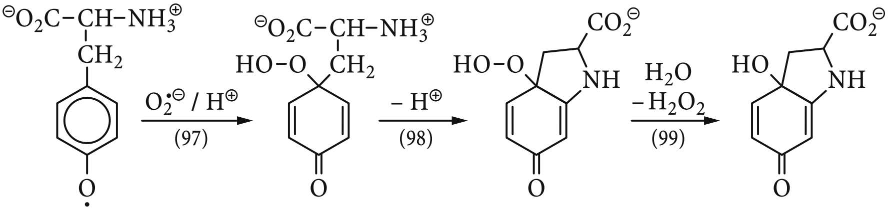
The value for k_{91} is 1.4×10^4 dm^3 mol^{-1} s^{-1}, and that for k_{94} is 5×10^4 dm^3 mol^{-1} s^{-1}. Kinetically, reactions (92) and (93) cannot be separated ($k_{93} + 0.36\ k_{92} = 1.2 \times 10^7$ dm^3 mol^{-1} s^{-1}).

The ascorbate radicals also react very rapidly with $O_2^{\bullet-}/HO_2^{\bullet}$ [reactions (95) and (96), $k_{95} = 5 \times 10^9$ dm^3 mol^{-1} s^{-1}, $k_{96} = 2.6 \times 10^8$ dm^3 mol^{-1} s^{-1}].

$$A^{\bullet-} + HO_2^{\bullet} \rightarrow \text{products} \tag{95}$$

$$A^{\bullet-} + O_2^{\bullet-} \rightarrow \text{products} \tag{96}$$

The ascorbate radical is one of the radicals that do not react readily with O_2, but it reacts with $O_2^{\bullet-}$. The product of this reaction is not yet known. There are other radicals that have similar properties such as phenoxyl-type radicals. A prominent member of this group is the vitamin E radical. In the phenoxyl radical series, addition as well as ET have been discussed (Jonsson et al. 1993; d'Alessandro et al. 2000). The reaction of the tyrosyl radical with $O_2^{\bullet-}$ is an example showing that addition is the main route despite of its relatively high redox potential [reactions (97)–(99); only one pathway is shown; Jin et al. 1993].



The *N*-centered tryptophan (Fang et al. 1998) and bisbenzimidazole radicals (Adhikary et al. 2000) also do not react with O_2, but readily with $O_2^{\bullet-}$, the former by addition. In the nucleobase series, a similar situation prevails for $G^{\bullet}$ ($k(G^{\bullet} + O_2^{\bullet-}) = 4.4 \times 10^9$ dm^3 mol^{-1} s^{-1}; von Sonntag 1994). Most of the reaction seems to occur by ET reforming G plus O_2, but in competition about 15% to lead to products such as Iz and 8-oxo-G (Misiaszek et al. 2004).

The $O_2^{\bullet-}/HO_2^{\bullet}$ radicals can be trapped by spin traps, but the rate constants are low and their lifetime is often only short (Lauricella et al. 2004), i.e., they give rise to the $^{\bullet}OH$-adduct radical upon hydrolysis (Chap. 3.4). To increase the lifetime of the DEPMPO adduct, it has been suggested to freeze the solution to liquid nitrogen temperature for detection (Dambrova et al. 2000).

8.12
The 'Haber-Weiss Reaction'

In their brilliant papers, Haber and Weiss (1932, 1934) studied the iron-catalyzed decomposition of H_2O_2 and proposed the reaction of $HO_2^\bullet$ with H_2O_2 as a single step [reaction (100)]. This has since been shown to proceed in two steps [reactions (101) and (102); Czapski and Ilan 1978; Bielski 1985; Rush and Bielski 1985].

$$HO_2^\bullet + H_2O_2 \rightarrow H_2O + O_2 + {}^\bullet OH \quad (100)$$

$$HO_2^\bullet + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+ \quad (101)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \quad (102)$$

The latter is well known as 'Fenton reaction' (Fenton and Jackson 1899). Over the years, the 'Haber-Weiss reaction' [reaction (100)] has often been assumed to be the source of $^\bullet OH$. The much greater likelihood of transition metal catalysis, which is also possible in biological systems, has often been overlooked. Traces of transition metal ions may be present in otherwise pure model systems (Fridovich and Porter 1981), and may even be leached out of the glassware (Ulanski et al. 1996c). It is now clear that the uncatalyzed reaction (100) is slow [$k = 0.2\ dm^3\ mol^{-1}\ s^{-1}$; Ferradini and Seide 1969; $k = 0.5\ dm^3\ mol^{-1}\ s^{-1}$, $k(O_2^{\bullet -} + H_2O_2) = 0.13 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$; Weinstein and Bielski 1979] and can be neglected for the majority of experimental conditions. The thermodynamics of the uncatalyzed and catalyzed 'Haber-Weiss reaction' has been discussed in some detail by Koppenol (1983).

In contrast to the Haber-Weiss reaction, the reaction of $O_2^{\bullet -}$ with HOCl [reaction (103)] proceeds without transition metal catalysis (Candeias et al. 1993).

$$HOCl + O_2^{\bullet -} \rightarrow {}^\bullet OH + Cl^- + O_2 \quad (103)$$

This reaction is considered to be an important step in the phagocytic killing of microorganisms by free-radical processes (Saran et al. 1999). In this reaction, also $Cl^\bullet$ was considered to play a role (for the complexities of $^\bullet OH/Cl^-$ reactions in aqueous solution, see Yu and Barker 2003a,b; Yu et al. 2004).

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