5

Inorganic Radicals

5.1
General Remarks

Reactive free radicals such as $^{\bullet}OH$ or the e_{aq}^{-} react with many inorganic anions leading to inorganic radicals which have properties not given by the precursor radicals. For this reason, these inorganic radicals have been used with advantage, also in DNA research, to create and study free-radical intermediates otherwise either not accessible or only formed in low yields in competition with other reactions. A typical example is the specific formation of damaged G sites in DNA by using inorganic radicals as the oxidant (Martin and Anderson 1998; Milligan et al. 2000, 2002; Chap. 12.3).

5.2
Formation of Inorganic Radicals and Their Dimeric Radical Anions

Hydroxyl radicals react with many halide (pseudohalide) ions at close to diffusion-controlled rates thereby forming a three-electron-bonded adduct radical [e.g., reaction (1); $k = 1.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1}; Zehavi and Rabani 1972]. These adducts may decompose into OH^- and the halide (pseudohalide) radical which then complexes with another halide (pseudohalide) ion yielding the dihalogen radical anion [reactions (2) and (3); $k_2 = 4.2 \times 10^6$ s^{-1}; $k_3 \approx 10^{10}$ dm^3 mol^{-1} s^{-1}; for resonance Raman spectra of such intermediates, see Tripathi et al. 1985].

$$^{\bullet}OH + Br^- \rightarrow HOBr^{\bullet -} \tag{1}$$

$$HOBr^{\bullet -} \rightarrow Br^{\bullet} + OH^- \tag{2}$$

$$Br^{\bullet} + Br^- \rightleftharpoons Br_2^{\bullet -} \tag{3}$$

They are held together via a weak σσ* three-electron bond. This mechanism adequately describes the reactions of Br^-, I^-, SCN^- and N_3^-. Equilibrium constants are compiled in Table 5.1, where it can be seen that even at moderate halide (pseudohalide) concentrations the equilibrium is shifted to the right [cf. reaction (3); for a direct determination of the forward reaction, see Nagarajan and Fessenden 1985].

A number of mixed complexes have also been characterized (Schöneshöfer and Henglein 1969, 1970; Schöneshöfer 1969, 1973; Ershov et al. 2002). In this context, it is interesting that $Cl^{\bullet}$ also undergoes a weak three-electron bond with water (Sevilla et al. 1997).

Similar hypervalent iodine radicals (9–I–2) are formed in the reaction of alkyl radicals with alkyliodides ($R^{\bullet} + RI \rightarrow R_2I^{\bullet}$), and as an intramolecular complex they are stable enough that a reaction with O_2 is only low (Miranda et al. 2000). Such 9–X–2 radicals have also been postulated as intermediates in the reduction of alkylhalides by α-hydroxyalkyl radicals (Lemmes and von Sonntag 1982).

Table 5.1. Compilation of equilibrium constants of some dimeric radical anions

Dimeric radical anion	Equilibrium constant/dm^3 mol^{-1}	Reference
$Cl_2^{\bullet-}$	6.0×10^4 1.4×10^5	Buxton et al. (1998); Yu and Barker (2003)
$Br_2^{\bullet-}$	3.9×10^5	Liu et al. (2002)
$I_2^{\bullet-}$	1.1×10^5	Baxendale et al. (1968); Schwarz and Bielski (1986)
$(SCN)_2^{\bullet-}$	2×10^5	Baxendale et al. (1968); Buxton and Stuart (1995)
$N_6^{\bullet-}$	0.33	Alfassi et al. (1986)

In basic and neutral solutions, $Cl^\bullet$ is a stronger oxidant than $^\bullet OH$ (cf. Table 5.2), and the formation of $Cl_2^{\bullet-}$ only proceeds in acid solution [reactions (4) and (5); Anbar and Thomas 1964]. Details of this very complex situation and the involvement of equilibrium (6) have been redetermined (Buxton et al. 1998). It is evident that the even more strongly oxidizing fluorine atom cannot be produced this way.

$$^\bullet OH + Cl^- \rightleftharpoons HOCl^{\bullet-} \tag{4}$$

$$HOCl^{\bullet-} + H^+ \rightarrow H_2O + Cl^\bullet \tag{5}$$

$$Cl^\bullet + Cl^- \rightleftharpoons Cl_2^{\bullet-} \tag{6}$$

An exception is the reaction of $^\bullet OH$ with the cyanide ion. Its $^\bullet OH$ adduct rapidly protonates even at high pH, but in this reaction the cyanide radical is not formed because of its very high reduction potential (Wardman 1989). It rather undergoes an enol→keto tautomerization [overall reaction (7); Behar and Fessenden 1972; Behar 1974; Büchler et al. 1976; Bielski and Allen 1977; Muñoz et al. 2000].

$$^\bullet OH + CN^- + H_2O \rightarrow {}^\bullet C(O)NH_2 \tag{7}$$

Since bicarbonate/carbonate are omnipresent, it is of special interest that $^\bullet OH$ also reacts with these ions, yielding the oxidizing $CO_3^{\bullet-}$ radical [reactions (8 and 9); $k_8 = 3.9 \times 10^8$ dm^3 mol^{-1} s^{-1}, $k_9 = 8.5 \times 10^6$ dm^3 mol^{-1} s^{-1}; Buxton and Elliot 1986], i.e. bicarbonate is about 40 times less reactive.

$$^\bullet OH + CO_3^{2-} \rightarrow OH^- + CO_3^{\bullet-} \tag{8}$$

$$^{\bullet}OH + HCO_3^- \rightarrow H_2O + CO_3^{\bullet -} \tag{9}$$

The $CO_3^{\bullet -}$ radical is characterized by a strong absorption at 600 nm ($\varepsilon \approx 2000$ dm^3 mol^{-1} cm^{-1}) (Weeks and Rabani 1966; Zuo et al. 1999). This absorption does not change between pH 0 and 13 (Czapski et al. 1999; Zuo et al. 1999; see, however, Eriksen et al. 1985). Nevertheless, the pK_a value of $HCO_3^{\bullet}$ [equilibrium (10)] continues to be debated, and pK_a values between 7 and 9.6 have been reported (Chen and Hoffman 1972; Chen et al. 1973; Eriksen et al. 1985; Zuo et al. 1999). However, there is now increasing evidence (Bisby et al. 1998; Czapski et al. 1999) that it must be much lower, <0 (Czapski et al. 1999), and hence it is more acidic than its parent [p$K_a(H_2CO_3) = 3.5$]. For a detailed discussion, see Czapski et al. (1999).

$$HCO_3^{\bullet} \rightleftharpoons H^+ + CO_3^{\bullet -} \tag{10}$$

The reaction of $^{\bullet}OH$ with nitrite yields $^{\bullet}NO_2$ [reaction (11); $k \approx 1 \times 10^{10}$ dm^3 mol^{-1} s^{-1}], but also the reaction of e_{aq}^- with nitrate leads to $^{\bullet}NO_2$ via a short-lived adduct, $NO_3^{\bullet 2-}$ [reaction (12); $k = 9.7 \times 10^9$ dm^3 mol^{-1} s^{-1}]. The latter subsequently decays into $^{\bullet}NO_2$ [reaction (13); $k = 4.6 \times 10^3$ s^{-1}; Alfassi et al. 1998].

$$^{\bullet}OH + NO_2^- \rightarrow OH^- + {}^{\bullet}NO_2 \tag{11}$$

$$e_{aq}^- + NO_3^- \rightarrow NO_3^{\bullet 2-} \tag{12}$$

$$NO_3^{\bullet 2-} + H_2O \rightarrow {}^{\bullet}NO_2 + 2OH^- \tag{13}$$

The sulfate radical anion, $SO_4^{\bullet -}$, can be formed from peroxodisulfate, $S_2O_8^{2-}$, photolytically [reaction (14)] or by its reaction with e_{aq}^- [reaction (15); $k = 1.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}] and $^{\bullet}H$ [reaction (6); $k = 1.4 \times 10^7$ dm^3 mol^{-1} s^{-1}]. For the photolytic generation, one has to take into account that peroxodisulfate absorbs only weakly in the UV with absorption coefficients very close to that of H_2O_2 (Chap. 2.4). However, its decomposition can be sensitized by triplet acetone (acetone reacts only slowly with $SO_4^{\bullet -}$). As measured by photoacoustic calorimetry, the reaction volume and enthalpy changes for reaction (14) are 8.9 ml mol^{-1} and 120 kJ mol^{-1}, respectively (Brusa et al. 2000). Compared to H_2O_2, peroxodisulfate has a rather weak O–O bond, and this is reflected by its ready cleavage which can also be induced thermally (Strasko et al. 2000) at temperatures, where H_2O_2 does not yet show any noticeable decomposition (Chap. 2.4).

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{\bullet -} \tag{14}$$

$$S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4^{\bullet -} + SO_4^{2-} \tag{15}$$

$$S_2O_8^{2-} + {}^{\bullet}H \rightarrow SO_4^{\bullet -} + HSO_4^- \tag{16}$$

The $SO_4^{\bullet -}$ radical is one of the strongest oxidants (cf. Table 5.2), and in the presence of Cl^- it is in equilibrium with $Cl^{\bullet}$ [reaction (17); $K = 2.9$ (Buxton et al. 1999), $K = 1.5$ (Yu et al. 2004)].

$$SO_4^{\bullet-} + Cl^- \rightleftharpoons SO_4^{2-} + {}^{\bullet}Cl \quad (17)$$

The phosphate radical, $PO_4^{\bullet 2-}$, is related to $SO_4^{\bullet-}$. It may be similarly generated photolytically or radiolytically from peroxodiphosphate (Maruthamuthu and Neta 1977, 1978; Maruthamuthu 1980; Kumar and Adinarayana 2000). Its reduction potential is lower than that of $SO_4^{\bullet-}$, that is, the latter reacts with phosphate, although the rate of reaction is only slow (with HPO_4^{2-} $k = 1.2 \times 10^6$ dm^3 mol^{-1} s^{-1}, with $H_2PO_4^-$ $k < 7 \times 10^4$ dm^3 mol^{-1} s^{-1}; Maruthamuthu and Neta 1978). Its reactions are of some interest in the context of DNA free-radical chemistry, since in DNA this type of radical may be formed upon oxidation of the phosphate groups, for example, by ionizing radiation (direct effect) or photoionization at short wavelengths.

The $H_2PO_4^{\bullet}$ radical has pK_a values of 5.7 and 8.9, and the oxidation power decreases in the order $SO_4^{\bullet-} > H_2PO_4^{\bullet} > HPO_4^{\bullet-} > PO_4^{\bullet 2-}$ (Maruthamuthu and Neta 1978). The $H_2PO_4^{\bullet}$ radicals abstract H-atoms at slightly higher rates than $SO_4^{\bullet-}$, and in their addition reactions they are similarly electrophilic ($\rho = -1.8$) as the $SO_4^{\bullet-}$ radical (Maruthamuthu and Neta 1977).

When generating the di(pseudo)halide radical anions radiolytically, one has to keep in mind that the halide ions do not react with $^{\bullet}H$, but HN_3/N_3^- does. Originally, it has been suggested that $N_3^{\bullet}$ and H_2 are formed (Alfassi et al. 1986), but it was later shown that it reacts according to reaction (18) (Deeble et al. 1990).

$$^{\bullet}H + N_3^- + H^+ \rightarrow {}^{\bullet}NH_2 + N_2 \quad (18)$$

The $SeO_3^{\bullet-}$, a Se(V) species with a high redox potential (cf. Table 5.2) can be produced radiolytically from Se(VI) upon reduction by e_{aq}^- [reaction (19)] and from Se(IV) by $^{\bullet}OH$ [reaction (20); Kläning and Sehested 1986].

$$SeO_4^{2-} + e_{aq}^- \rightarrow SeO_3^{\bullet-} \quad (19)$$

$$SeO_3^{2-} + {}^{\bullet}OH \rightarrow SeO_3^{\bullet-} + OH^- \quad (20)$$

The $SeO_3^{\bullet-}$ radical has been used with advantage to oxidize DNA specifically at G sites (Martin and Anderson 1998; Milligan et al. 2002).

The strongly oxidizing $^{\bullet}NO_3$ radical ($E^0 = 2.0$ V vs. SCE in acetonitrile) can be generated photolytically in acetonitrile [reaction (21)].

$$(NH_4)_2Ce(NO_3)_6 + h\nu \rightarrow {}^{\bullet}NO_3 + (NH_4)_2Ce(NO_3)_5 \quad (21)$$

It has been used to study the oxidative cleavage of Thy dimers (Krüger and Wille 2001; Chap. 10.14).

All these radicals have oxidizing properties, but there are also some inorganic radicals which have reducing properties (E < 0 V; cf. Table 5.2).

For example, H-abstraction from formate [reaction (22)], addition of $^{\bullet}OH$ to CO [reaction (23)] or the reaction of e_{aq}^- with CO_2 [reaction (24)] yields the (reducing) $CO_2^{\bullet-}$ radical. The pK_a value of its conjugate acid $^{\bullet}CO_2H$ [equilibrium (25)] continues to be in dispute. Using different approaches to determine its pK_a,

Table 5.2. Compilation of the reduction potentials of some inorganic radicals; values selected by Wardman (1989). For further data, see also Das et al. (1999)

Couple	E/V
$F^{\bullet}/F^-$	+3.60
$^{\bullet}OH, H^+/H_2O$	+2.73
$Cl^{\bullet}/Cl^-$	+2.60
$SO_4^{\bullet-}/SO_4^{2-}$	+2.47
$Cl_2^{\bullet-}/2Cl^-$	+2.30
$Br^{\bullet}/Br^-$	+2.00
$^{\bullet}OH/OH^-$	+1.90
$O_3, H^+/HO_3^{\bullet}$ (pH 7)	+1.80
$SeO_3^{\bullet-}/SeO_3^{2-}$ (pH 7)	+1.77
$Br_2^{\bullet-}/2\,Br^-$	+1.60
$CO_3^{\bullet-}/CO_3^{2-}$	+1.59
$I^{\bullet}/I^-$	+1.40
$HO_2^{\bullet}, H^+/H_2O_2$ (pH 0)	+1.48
$(SCN)_2^{\bullet-}/2SCN^-$	+1.33
$N_3^{\bullet}/N_3^-$	+1.30
$^{\bullet}SH/SH^-$	+1.15
$O_3/O_3^{\bullet-}$ (pH 11-12)	+1.01
$I_2^{\bullet-}/2I^-$	+1.05
$NO_2^{\bullet}/NO_2^-$	+1.00
$HO_2^{\bullet}/HO_2^-$	+0.79
$O_2(^1\Delta_g)/O_2^{\bullet-}$	+0.65
$O_2/O_2^{\bullet-}$	−0.33*
$CO_2/CO_2^{\bullet-}$	−1.90
aq/e_{aq}^-	−2.87

* This reduction potential relates, by definition, to O_2-saturated solutions. For comparison with other values that are based on molarity, a value of −0.179 V should be taken (Wardman 1991).

values of 3.9 (Fojtik et al. 1970), 2.3 (Flyunt et al. 2001), 1.4 (Buxton and Sellers 1973) and −0.4 (Jeevarajan et al. 1990) are reported in the literature. The reason for these large discrepancies is not yet known. Nevertheless, the majority of these values suggest that $^{\bullet}CO_2H$ is more acidic than its parent, formic acid (pK_a = 3.75).

$$^{\bullet}OH\ (H^{\bullet}) + HCO_2^{-} \rightarrow H_2O\ (H_2) + CO_2^{\bullet -} \tag{22}$$

$$^{\bullet}OH + CO \rightarrow {}^{\bullet}CO_2H \tag{23}$$

$$e_{aq}^{-} + CO_2 \rightarrow CO_2^{\bullet -} \tag{24}$$

$$^{\bullet}CO_2H \rightleftharpoons CO_2^{\bullet -} + H^{+} \tag{25}$$

In radiolytic studies, $CO_2^{\bullet -}$ is often used with some advantage as a precursor of the superoxide radical, $O_2^{\bullet -}$ [reaction (26); Chap. 8.4].

$$CO_2^{\bullet -} + O_2 \rightarrow CO_2 + O_2^{\bullet -} \tag{26}$$

5.3 Reduction Potentials of Inorganic Radicals

The redox properties of the inorganic radicals (for a compilation see Table 5.2) have been widely used to produce specifically certain radicals, notably radical cations and radical anions. It is worth mentioning that $^{\bullet}OH$, although it has a high redox potential, normally undergoes addition rather than one-electron transfer (ET) reactions (Chap. 3).

5.4 Reactions of Inorganic Radicals with Organic Substrates

In DNA free-radical chemistry, the strongly oxidizing radicals, notably $SO_4^{\bullet -}$, $Br_2^{\bullet -}$ and $N_3^{\bullet}$, and transition-metal ions in high oxidation states, such as Tl^{2+}, have often been used to produce one-electron-oxidized intermediates (Chap. 10.2). These inorganic radicals react very rapidly with many organic substrates by forming adduct radicals. In the case of $SO_4^{\bullet -}$, for example, an adduct to a C–C double bond may precede ET. In fact, in the reaction with simple olefins, such adduct radicals have been detected by EPR (Davies and Gilbert 1984). They also may form adducts via σσ* three-electron bonds, notably at sulfur and even nitrogen. Typical examples are the oxidation of thiolates by $Br_2^{\bullet -}$ or $I_2^{\bullet -}$ forming $RSBr^{\bullet -}$ ($RSI^{\bullet -}$) as short-lived intermediates (Packer 1984) or with sulfides such as methionine (Hiller and Asmus 1981; Champagne et al. 1991). In proteins, $Br_2^{\bullet -}$ has been used to study the transformation of the methionyl radical into the tyrosyl radical (Prütz et al. 1985a), and such an adduct must be formed in the first step.

Although $Br_2^{•-}$ has a higher redox potential than $N_3^•$, it reacts notably slower (Neta et al. 1988). An explanation for this is provided by the Marcus theory for outer-sphere ET (Marcus 1993, 1999). According to this theory, the rate constant for ET between two redox partners, **A** and **B**, is given approximately by the simple expression $k = (k_{ex,A} \times k_{ex,B} \times K_{A,B})^{1/2}$, where $k_{ex,A}$ and $k_{ex,B}$ are the rate constants for self-exchange for the two redox couples and $K_{A,B}$ is the equilibrium constant of the redox reaction. Clearly, for a common redox couple **A**, the rate constant will increase with increasing $K_{A,B}$, i.e., increasing redox potential of redox couple **B** and also with increasing $k_{ex,B}$. The value of k_{ex} for $Br_2^{•-}/2Br^-$ is so much smaller than that for $N_3^•/N_3^-$ that this effect outweighs by far the reverse effect of $K_{A,B}$. In addition, $N_3^•$ appears in many cases to oxidize by way of an inner-sphere ET, which further increases the rate beyond what the Marcus theory would predict. As for experimental values for k_{ex} of main-group redox couples, only very few of them are known. One such couple is $O_2^{•-}/O_2$ for which k_{ex} has been determined to be 450 ± 160 (Lind et al. 1989). However, employing certain molecular parameters, such as bond lengths, vibration frequencies, ionic radii, etc., more or less accurate values for k_{ex} can be predicted by use of the Marcus theory.

The $^•NO_2$ radical (and also the $CO_3^{•-}$ radical) are of some biological interest (Augusto et al. 2002) because they play some role in the reactions of peroxynitrite (Chap. 2.4). For example, $^•NO_2$ oxidizes tyrosine to nitrotyrosine (Prütz et al. 1985b), and the latter has been considered a promoter of free-radical damage in DNA model systems (Prütz 1986). In this context, it may be of interest that $CO_3^{•-}$ reacts with a self-complementary ODN ($k = 1.9 \times 10^7$ dm^3 mol^{-1} s^{-1}) exclusively at G (by ET) (Chap. 11.2).

The dihalogen radical anions are electrophilic radicals [a correlation with the σ values of aromatic compounds gives $\rho = -1.5$ for $Cl_2^{•-}$ (Hasegawa and Neta 1978) and $\rho = -1.1$ for $Br_2^{•-}$ (Kemsley et al. 1974)]. The temperature dependence of the rates of reaction of these and other inorganic radicals have been measured (Alfassi et al. 1990). The rates of reaction do not seem to correlate with the exothermicity of the reactions. The variations in the rate constants appear more strongly dependent on changes in the pre-exponential factors rather than on changes in the activation energy.

Although the dihalogen radical anions mainly act as oxidants, in the reaction of $Br_2^{•-}$ with phloroglucinol as much as 8% bromination has been observed (Wang et al. 1994), and in the reaction of $Cl_2^{•-}$ with fumaric acid the chlorine atom adduct has been detected by EPR (Chawla and Fessenden 1975). When their rate constant with a given substrate is low, it is also possible that the observed products are due to the reaction of the halogen atom which is always in equilibrium with dihalogen radical anion. A case in point may be the reaction of $Br_2^{•-}$ with the pyrimidines (Cadet et al. 1983) and the reactions of $Cl_2^{•-}/Cl^•$ with *t*BuOH (Mertens 1994), where the observed rate of reaction is very low (Hasegawa and Neta 1978), and even with benzene under certain conditions (Alegre et al. 2000; for a discussion of chlorine atom reactions in organic solvents, see Ingold et al. 1990).

With alcohols, the $SO_4^{\bullet -}$ radical reacts by H-abstraction rather than by ET (Eibenberger et al. 1978). These reactions are rather slow (e.g., with *t*BuOH $k = 8 \times 10^5$ dm^3 mol^{-1} s^{-1}; Redpath and Willson 1975; Buxton et al. 1999), and thus $SO_4^{\bullet -}$ is considerably more selective than $^{\bullet}OH$ (Gilbert et al. 1999). $SO_4^{\bullet -}$ is always generated from $S_2O_8^{2-}$, and like H_2O_2 this peroxide readily reacts with reducing radicals such as derived from primary and secondary alcohols thereby inducing chain reactions with complex kinetics (Schuchmann and von Sonntag 1988; Ulanski and von Sonntag 1999) but also with those derived from the pyrimidine nucleobases (Chap. 10.2).

References

Alegre ML, Geronés M, Rosso JA, Bertolotti SG, Braun AM, Mártiere DO, Gonzales MC (2000) Kinetic study of the reactions of chlorine atoms and $Cl_2^{\bullet -}$ radical anions in aqueous solutions. I. Reaction with benzene. J Phys Chem A 104:3117–3125

Alfassi ZB, Prütz WA, Schuler RH (1986) Intermediates in the oxidation of azide ion in acidic solutions. J Phys Chem 90:1198–1203

Alfassi ZB, Huie RE, Neta P, Shoute LCT (1990) Temperature dependence of the rate constants for reaction of inorganic radicals with organic reductants. J Phys Chem 94:8800–8805

Alfassi ZB, Dhanasekaran T, Huie RE, Neta P (1998) On the reactions of $CO_3^{\bullet -}$ radicals with NO_x radicals. Radiat Phys Chem 56:475–482

Anbar M, Thomas JK (1964) Pulse radiolysis studies of aqueous sodium chloride solutions. J Phys Chem 68:3829–3835

Augusto O, Bonini MG, Amanso AM, Linares E, Santos CCX, de Menezes SL (2002) Nitrogen dioxide and carbonate radical anion: two emerging radicals in biology. Free Rad Biol Med 32:841–859

Baxendale JH, Bevan PLT, Stott DA (1968) Pulse radiolysis of aqueous thiocyanate and iodide solutions. Trans Faraday Soc 64:2389–2397

Behar D (1974) Pulse radiolysis study of aqueous hydrogen cyanide and cyanide solutions. J Phys Chem 78:2660–2663

Behar D, Fessenden RW (1972) An electron spin resonance investigation of the reactions in irradiated aqueous solutions of hydrogen cyanide and the cyanide ion. J Phys Chem 76:3945–3950

Bielski BHJ, Allen AO (1977) Radiation chemistry of aqueous cyanide ion. J Am Chem Soc 99:5931–5934

Bisby RH, Johnson SA, Parker AW, Tavender SM (1998) Time–resolved resonance Raman spectroscopy of the carbonate radical. J Chem Soc Faraday Trans 94:2069–2072

Brusa MA, Churio MS, Grela MA, Bertolotti SG, Previtali CM (2000) Reaction volume and reaction enthalpy upon aqueous peroxodisulfate dissociation: $S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -}$. Phys Chem Chem Phys 2:2383–2387

Buxton GV, Elliot AJ (1986) Rate constant for reaction of hydroxyl radicals with bicarbonate ions. Radiat Phys Chem 27:241–243

Buxton GV, Sellers RM (1973) Acid dissociation constant of the carboxyl radical. Pulse radiolysis studies of aqueous solutions of formic acid and sodium formate. J Chem Soc Faraday Trans 1 69:555–559

Buxton GV, Stuart CR (1995) Re–evaluation of the thiocyanate dosimeter for pulse radiolysis. J Chem Soc Faraday Trans 91:279–281

Buxton GV, Bydder M, Salmon GA (1998) Reactivity of chlorine atoms in aqueous solution, part I. The equilibrium $Cl^{\bullet} + Cl^- = Cl_2^{\bullet -}$. J Chem Soc Faraday Trans 94:653–657

Buxton GV, Bydder M, Salmon GA (1999) The reactivity of chlorine atoms in aqueous solution, part II. The equilibrium $SO_4^{\bullet -} + Cl^- = Cl^{\bullet} + SO_4^{2-}$. Phys Chem Chem Phys 1:269–273

Büchler H, Bühler RE, Cooper R (1976) Pulse radiolysis of aqueous cyanide solutions. Kinetics of the transient OH and H adducts and subsequent rearrangements. J Phys Chem 80:1549–1553

Cadet J, Voituriez L, Berger M, Myers LS Jr (1983) Radiation-induced degradation of purine and pyrimidine 2′-deoxyribonucleosides in aqueous KBr solutions. Z Naturforsch 38b:1643-1651

Champagne MH, Mullins MW, Colson A-O, Sevilla MD (1991) Electron spin resonance evidence for intra- and intermolecular σσ* bonding in methionine radicals: relative stabilities of S-Cl, S-Br, S-N, and S-S three electron bonds. J Phys Chem 95:6487–6493

Chawla OP, Fessenden RW (1975) Electron spin resonance and pulse radiolysis studies of some reactions of $SO_4^{\bullet-}$. J Phys Chem 79:2693–2700

Chen S-N, Hoffman MZ (1972) Acid-base properties of the CO_3^- radical in aqueous solution. J Chem Soc Chem Commun 17:991

Chen S, Cope VW, Hoffmann MZ (1973) Behavior of CO_3^- radicals generated in the flash photolysis of carbonatoamine complexes of Cobalt(III) in aqueous solution. J Phys Chem 77:1111–1116

Czapski G, Lymar SV, Schwarz HA (1999) Acidity of the carbonate radical. J Phys Chem A 103:3447–3450

Das TN, Huie RE, Neta P (1999) Reduction potentials of $SO_3^{\bullet-}$, $SO_5^{\bullet-}$, and $S_4O_6^{\bullet 3-}$ radicals in aqueous solution. J Phys Chem A 103:3581–3588

Davies MJ, Gilbert BC (1984) Electron spin resonance studies, part 68. Addition versus overall one-electron abstraction in the oxidation of alkenes and dienes by $SO_4^{-\bullet}$, $Cl_2^{-\bullet}$, and $^{\bullet}OH$ in acidic aqueous solution. J Chem Soc Perkin Trans 2 1809–1815

Deeble DJ, Parsons BJ, Johnson GRA (1990) Reactions of the hydrogen atom with azide, bromide and iodide ions in aqueous solution. Radiat Phys Chem 36:487–491

Eibenberger H, Steenken S, O'Neill P, Schulte-Frohlinde D (1978) Pulse radiolysis and E.S.R. studies concerning the reaction of $SO_4^{-\bullet}$ with alcohols and ethers in aqueous solution. J Phys Chem 82:749–750

Eriksen TE, Lind J, Merényi G (1985) On the acid-base equilibrium of the carbonate radical. Radiat Phys Chem 26:197–199

Ershov BG, Kelm M, Gordeev AV, Janata E (2002) A pulse radiolysis study of the oxidation of Br^- by $Cl_2^{\bullet-}$ in aqueous solution: formation and properties of $ClBr^{\bullet-}$. Phys Chem Chem Phys 4:1872–1875

Flyunt R, Schuchmann MN, von Sonntag C (2001) Combination vs. proton-catalysed disproportionation of the carboxyl radical anion, $CO_2^{\bullet-}$, in aqueous solution. Chem Eur J 7:796–799

Fojtik A, Czapski G, Henglein A (1970) Pulse radiolytic investigation of the carboxyl radical in aqueous solution. J Phys Chem 74:3204–3208

Gilbert BC, Lindsay Smith JR, Taylor P, Ward S, Withwood AC (1999) The interplay of electronic, steric and stereoelectronic effects in hydrogen-atom abstraction reactions of SO_4^-, revealed by EPR spectroscopy. J Chem Soc Perkin Trans 2 1631–1637

Hasegawa K, Neta P (1978) Rate constants and mechanisms of reaction of Cl_2^- radicals. J Phys Chem 82:856–859

Hiller K-O, Asmus K-D (1981) Oxidation of methionine by X_2^- in aqueous solution and characterization of some S therefore X three-electron bonded intermediates. A pulse radiolysis study. Int J Radiat Biol 40:583–595

Ingold KU, Lusztyk J, Raner KD (1990) The unusual and the unexpected in an old reaction. The photochloronation of alkanes with molecular chlorine in solution. Acc Chem Res 23:219–225

Jeevarajan AS, Carmichael I, Fessenden RW (1990) ESR Measurement of the pK of caboxyl radical and ab calculation of the carbon-13 hyperfine constant. J Phys Chem 94:1372–1376

Kemsley KG, Moore JS, Phillips GO, Sosnowski A (1974) Reaction of radical probes with substituted phenols as models for the investigation of tyrosine in aldolase and chemically modified aldolase. Acta Vitaminol Enzymol 28:263–267

Kläning UK, Sehested K (1986) Selenium(V). A pulse radiolysis study. J Phys Chem 90:5460–5464

Krüger O, Wille U (2001) Oxidative cleavage of a cyclobutane pyrimidine dimer by photochemically generated nitrate radicals ($NO_3^{\bullet}$). Org Lett 10:1455–1458

Kumar MR, Adinarayana M (2000) Kinetics and mechanism of protection of thymine from phosphate radical anion under anoxic conditions. Int J Chem Kinet 271–275

Lemmes R, von Sonntag C (1982) On the formation of deoxy sugars from halogenated carbohydrates by α-hydroxyalkyl radicals: considerations for the optimisation of reaction conditions. Carbohydr Res 105:276–282

Lind J, Shen X, Merényi G, Jonsson B (1989) Determination of the rate constant of self-exchange of the $O_2/O_2^{\bullet-}$ couple in water by $^{18}O/^{16}O$ isotope marking. J Am Chem Soc 111:7654–7655
Liu Y, Pimentel AS, Antoku Y, Barker JR (2002) Temperature-dependent rate and equilibrium constants for $Br^{\bullet}(aq) + Br^{-}(aq) \Leftrightarrow Br_2^{-\bullet}$ (aq). J Phys Chem A 106:11075–11082
Marcus RA (1993) Elektronentransferreaktionen in der Chemie – Theorie und Experiment (Nobel Vortrag). Angew Chem 105:1161–1172
Marcus RA (1999) Electron transfer past and future. In: Jortner J, Bixon M (eds) Electron transfer – from isolated molecules to biomolecules, part 1. Wiley, New York, pp 1–6
Martin RF, Anderson RF (1998) Pulse radiolysis studies indicate that electron transfer is involved in radioprotection by Hoechst 33342 and methylproamine. Int J Radiat Oncol Biol Phys 42:827–831
Maruthamuthu P (1980) Absolute rate constants for the reactions of sulfate, phosphate and hydroxyl radicals with monomers. Macromol Chem Rapid Commun 1:23–25
Maruthamuthu P, Neta P (1977) Reactions of phosphate radicals with organic compounds. J Phys Chem 81:1622–1625
Maruthamuthu P, Neta P (1978) Phosphate radicals. Spectra, acid-base equilibria, and reactions with inorganic compounds. J Phys Chem 82:710–713
Mertens R (1994) Photochemie und Strahlenchemie von organischen Chlorverbindungen in wässriger Lösung. Thesis, dissertation, Ruhr University, Bochum.
Milligan JR, Aguilera J, Paglinawan RA, Ward JF (2000) Mechanism of DNA damage by thiocyanate radicals. Int J Radiat Biol 76:1305–1314
Milligan JR, Aguilera J, Paglinawan RA, Ward JF (2002) One-electron oxidation of plasmid DNA by selenium(V) species. Int J Radiat Biol 78:359–374
Miranda MA, Pérez-Prieto J, Font-Sanchis E, Scaiano JC (2000) Five-membered-ring 9–I–2 radicals: direct detection and comparison with other hypervalent iodine radicals. Org Lett 1:1587–1589
Muñoz F, Schuchmann MN, Olbrich G, von Sonntag C (2000) Common intermediates in the OH-radical-induced oxidation of cyanide and formamide. J Chem Soc Perkin Trans 2 655–659
Nagarajan V, Fessenden RW (1985) Flash photolysis of transient radicals. 1. X_2^- with X = Cl, Br, I, and SCN. J Phys Chem 89:2330–2335
Neta P, Huie RE, Ross AB (1988) Rate constants for reactions of inorganic radicals in aqueous solution. J Phys Chem Ref Data 17:1027–1284
Packer JE (1984) A reinvestigation of the oxidation of cysteine by $Br_2^{\bullet-}$ and $I_2^{\bullet-}$. Evidence for CyS$\therefore$.Br^- and CyS.$\therefore$.I^-. J Chem Soc Perkin Trans 2 1015–1024
Prütz WA (1986) Nitro-tyrosine as promoter of free radical damage in a DNA model system. Free Rad Res Commun 2:77–83
Prütz WA, Butler J, Land EJ (1985a) Methionyl $\rightarrow$ tyrosyl radical transitions initiated by $Br_2^{\bullet-}$ in peptide model systems and ribonuclease A. Int J Radiat Biol 47:149–156
Prütz WA, Mönig H, Butler J, Land E (1985b) Reactions of nitrogen dioxide in aqueous model systems: oxidation of tyrosine units in peptides and proteins. Arch Biochem Biophys 243:125–134
Redpath JL, Willson RL (1975) Chain reactions and radiosensitization: model enzyme studies. Int J Radiat Biol 27:389–398
Schöneshöfer M (1969) Pulsradiolytische Untersuchung des gemischten Radikal-Anion- Komplexes $ClSCN^-$. Int J Radiat Phys Chem 1:505–513
Schöneshöfer M (1973) Pulsradiolytische Untersuchung über die Bildung des Radikal-Anions $SCNS_2O_3^{2-}$. Ber Bunsenges Phys Chem 77:257–262
Schöneshöfer M, Henglein A (1969) Pulsradiolytische Untersuchung der Dissoziationsgleichgewichte des gemischten Radikal-Anion-Komplexes $BrSCN^-$. Ber Bunsenges Phys Chem 73:289–293
Schöneshöfer M, Henglein A (1970) Pulsradiolytische Untersuchung der Komplexe $ISCN^-$ und I_2SCN^-. Ber Bunsenges Phys Chem 74:393–398
Schuchmann H-P, von Sonntag C (1988) The oxidation of methanol and 2-propanol by potassium peroxodisulphate in aqueous solution: free-radical chain mechanisms elucidated by radiation-chemical techniques. Radiat Phys Chem 32:149–156
Schwarz HA, Bielski BHJ (1986) Reactions of HO_2 and O_2^- with iodine and bromine and I_2^- and I atom reduction potentials. J Phys Chem 90:1445–1448
Sevilla MD, Summerfield S, Eliezer I, Rak J, Symons MCR (1997) Interaction of the chlorine atom with water: ESR and ab initio MO evidence for three-electron ($\sigma^2\sigma^{*1}$) bonding. J Phys Chem A 101:2910–2915

Strasko A, Brezová V, Liptáková M, Savel J (2000) Thermally initiated radical reactions of $K_2S_2O_8$: EPR spin trapping investigations. Magn Reson Chem 38:957–962

Tripathi GNR, Schuler RH, Fessenden RW (1985) Time-resolved resonance Raman spectra of dihalide radical anions in aqueous solution. Chem Phys Lett 113:563–568

Ulanski P, von Sonntag C (1999) The OH-radical-induced chain reactions of methanol with hydrogen peroxide and with peroxodisulfate. J Chem Soc Perkin Trans 2 165–168

Wang D, György G, Hildenbrand K, von Sonntag C (1994) Free-radical-induced oxidation of phloroglucinol – a pulse radiolysis and EPR study. J Chem Soc Perkin Trans 2 45–55

Wardman P (1989) Reduction potentials of one-electron couples involving free radicals in aqueous solution. J Phys Chem Ref Data 18:1637–1755

Wardman P (1991) The reduction potential of benzyl viologen: an important reference compound for oxidant/radical redox couples. Free Radical Res Comnun 14:57–67

Weeks JL, Rabani J (1966) The pulse radiolysis of deaerated aqueous carbonate solutions. I. Transient optical spectrum and mechanism. II. pK for OH radicals. J Phys Chem 70:2100–2105

Yu X-Y, Barker JR (2003) Hydrogen peroxide photolysis in acidic solutions containing chloride ions. I. Chemical mechanism. J Phys Chem A 107:1313–1324

Yu X-Y, Bao ZC, Barker JR (2004) Free radical reactions involving $Cl^•$, $Cl_2^{•-}$, and $SO_4^{•-}$ in the 248 nm photolysis of aqueous solutions containing $S_2O_8^{2-}$ and Cl^-. J Phys Chem A 108:295–308

Zehavi D, Rabani J (1972) The oxidation of the bromide ion by hydroxyl radicals. J Phys Chem 76:312–319

Zuo Z, Cai Z, Katsumura Y, Chitose N, Muroya Y (1999) Reinvestigation of the acid-base equilibrium of the (bi)carbonate radical and pH dependence of its reactivity with inorganic reactants. Radiat Phys Chem 55:15–23