# Production of OH radicals in the autoxidation of the Fe(II)–EDTA system

**Irina L. Yurkova,† Heinz-Peter Schuchmann and Clemens von Sonntag ***

*Max-Planck-Institut für Strahlenchemie, P.O. Box 101365, D-45413 Mülheim, Germany*

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The autoxidation of oxygenated solutions of Fe(II)–EDTA containing dimethyl sulfoxide (DMSO) proceeds with the participation of the OH radical. Its presence as the crucial reactive intermediate has been established by the competition method based on the formation of methanesulfinic acid from DMSO as the reference. As competitors were used guanosine, methanol, *tert*-butyl alcohol, acetamide, and acetonitrile, whose rate constants span a range of almost three orders of magnitude. In the absence of competitors the yield of methanesulfinic acid is between 1/5 and 1/6 of the Fe(III) formed. Other products are formic acid and formaldehyde. The process of DMSO oxidation is essentially a chain reaction initiated by the OH radical which is at the same time one in a succession of several free-radical chain carriers, and in which the EDTA complex of Fe(II) also participates.

The autoxidation of organic substances in aqueous media in the presence of ferrous ion, especially in complexed form, has continued to attract interest for many years. The stage is set by the formation of a ligand–ferrous–dioxygen complex where the dioxygen can be attached in various ways depending on the nature of the ligand (*cf*. ref. 1). Autoxidation chemistry is initiated by the transformation of these complexes into oxidizing species, or their reaction with oxidizable substrates. With regard to the mechanism of these processes, it has been debated whether, or under which conditions, it is mediated by iron–oxo species containing higher-valent iron [*e.g.* ferryl (Ligand)-$Fe^{IV}$=O and perferryl (Ligand)$Fe^{V}$=O; here and in the following, the roman-numeral superscripts signify the formal oxidation state of the metal atom], or by the OH radical generated in the course of Fenton-type reactions (*cf*. ref. 2–5). Depending on the nature of the ligand, one or the other pathway may be realized (yet other pathways are not ruled out: *e.g.,* lipid peroxidation has been thought[6] to be initiated by a diiron(II,III)–dioxygen complex $L{\cdot}Fe^{II}O{-}OFe^{III}{\cdot}L$[7,8]). Complexes with bleomycin (*cf*. ref. 9–11) and certain bleomycin analogues (*cf*. ref. 12), as well as with porphyrins (*cf*. ref. 13, 14) provide examples for higher-valent-iron pathways (as also do mixed base–acid solvents, *e.g.* pyridine–acetic acid, "GIF chemistry" systems, *cf*. ref. 15, but see also ref. 16). Crucially, in these oxygenated systems in the presence of organic solutes (which includes any organic ligand) there usually exists the possibility of a web of chain reactions mediated by organic peroxyl radicals (see below). The important consequence of this is that the identity of the primary oxidizing species which initiates the autoxidation process may remain obscure.

The present work is focused on the autoxidative behaviour of the ferrous complex of ethylenediaminetetraacetic acid (EDTA) in the presence of various organic additives, as reflected by the nature and amount of the products generated in the reaction (endpoint: complete transformation of ferrous to ferric). EDTA–iron complex is industrially used in the removal of pollutants by catalytic oxidation (*cf*. ref. 17). Recently, on the basis of a kinetic study,[18] a mechanism of oxidation of EDTA–Fe(II) complex with dioxygen to the ferric complex has been put forward whose overall rate is pH-dependent. It consists of reactions (1)–(4) (disregarding protonation equilibria where the ligand carries acidic functions).

$$L{\cdot}Fe^{II}{\cdot}H_2O + O_2 \longrightarrow L{\cdot}Fe^{II}{\cdot}O_2 + H_2O \quad (1)$$

$$L{\cdot}Fe^{II}{\cdot}O_2 \longrightarrow L{\cdot}Fe^{III}O{-}O^{\bullet} \quad (2)$$

$$L{\cdot}Fe^{III}O{-}O^{\bullet} + L{\cdot}Fe^{II}{\cdot}H_2O \longrightarrow L{\cdot}Fe^{III}O{-}OFe^{III}{\cdot}L + H_2O \quad (3)$$

$$L{\cdot}Fe^{III}O{-}OFe^{III}{\cdot}L + 2\,H_2O + 2\,H^+ \longrightarrow 2\,L{\cdot}Fe^{III}{\cdot}H_2O + H_2O_2 \quad (4)$$

There was no evidence of the involvement of higher-valent iron–oxo species (*e.g*. ferryl $L{\cdot}Fe^{IV}$=O). The participation of the hydroperoxyl/superoxide radical postulated earlier (*cf*. refs. 17, 19), implying reactions (5)–(8), has been disclaimed.[18]

$$L{\cdot}Fe^{III}O{-}O^{\bullet} + H_2O \longrightarrow L{\cdot}Fe^{III}{\cdot}H_2O + O_2^{\bullet -} \quad (5)$$

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet} \quad (6)$$

$$L{\cdot}Fe^{II}{\cdot}H_2O + O_2^{\bullet -}\,(HO_2^{\bullet}) \longrightarrow L{\cdot}Fe^{III}O{-}O^-\,(L{\cdot}Fe^{III}OOH) + H_2O \quad (7)$$

$$L{\cdot}Fe^{III}O{-}O^-\,(L{\cdot}Fe^{III}OOH) + H_2O + H^+ \longrightarrow L{\cdot}Fe^{III}{\cdot}H_2O + HO_2^-\,(H_2O_2) \quad (8)$$

On the other hand, on the basis of the data in refs. 20, 21 ($O_2$ reference state: 1 molar in the solution) one calculates $\Delta G^\circ$ = +6.4 kcal mol$^{-1}$ for the process spanning reactions (1), (2), and (5). Thus ln $K = -\Delta G^\circ/RT = 10.9$, *i.e.* $K = 1.8 \times 10^{-5}$, at 20 °C. The rate constant for the reverse process [reactions (−5), (−2) and (−1)] is reported to be about $5 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$.[22] This implies a rate constant of about 90 dm$^3$ mol$^{-1}$ s$^{-1}$ for the formation of $O_2^{\bullet -}$ by the process spanning reactions (1), (2), and (5). This is close to the value of 110 dm$^3$ mol$^{-1}$ s$^{-1}$ reported for the rate constant of the oxidation of the iron(II)–EDTA complex by $O_2$.[22] This would appear to leave little room for a branching, between reactions (3) and (5), of the reaction pathways. Reactions (5)–(8) are known also to play a role with, *e.g.*, polyphosphate[23] or porphyrins[24] as ligands.

The appearance of hydrogen peroxide gives rise to the

† *Permanent address*: Radiation Chemistry Department, Byelorussian State University, 4, F. Skoryna Ave., Minsk 220080, Byelorussia.

production of OH radicals in a Fenton process, probably *via* a perhydroxo complex $L{\cdot}Fe^{II}{\cdot}H_2O_2$ which may become manifest as an oxidizing species if sufficiently long-lived (which depends on the nature of the complexing agent), or decompose giving rise to OH radical (*cf*. ref. 25, 26), reactions (9) and (10). Ferryl

$$L{\cdot}Fe^{II}{\cdot}H_2O + H_2O_2 \longrightarrow L{\cdot}Fe^{II}{\cdot}H_2O_2 + H_2O \quad (9)$$

$$L{\cdot}Fe^{II}{\cdot}H_2O_2 + H_2O \longrightarrow L{\cdot}Fe^{III}{\cdot}H_2O + {}^{\bullet}OH + OH^- \quad (10)$$

species have also been postulated as active intermediates (*cf*. ref. 22).

The identification of products from Fenton-type reactions (*cf*. ref. 26) and the EPR analysis of spin traps (*cf*. ref. 27) have been employed to discriminate between the OH radical and other oxidizing species. The interpretation of spin-trap studies is, however, complicated by the possibility that the OH-substituted aminoxyl radical might have been formed *via* oxidation of the aminoxyl to the radical cation with subsequent neutralization by hydroxide (*i.e*. hydrolysis).[27–29]

The present study monitors the autoxidation process using dimethyl sulfoxide as a competitor with a series of compounds that react with the OH radical at widely different specific rates. The reactions involved include H-atom abstraction and OH-radical addition. Dimethyl sulfoxide is considered to be a specific reagent for probing the OH radical in aqueous solution. The main process is by reaction (11)[30,31] which gives rise to

$$(CH_3)_2SO + {}^{\bullet}OH \longrightarrow CH_3SO_2H + {}^{\bullet}CH_3 \quad (11)$$

methanesulfinic acid [92%;[30] the rest is H-atom abstraction from methyl, reaction (12)]. Its product, methanesulfinic acid, is

$$(CH_3)_2SO + {}^{\bullet}OH \longrightarrow {}^{\bullet}CH_2S(O)CH_3 + H_2O \quad (12)$$

conveniently determined colorimetrically[32,33] or by ion chromatography (this study).

The appearance of methyl radical leads to the formation of secondary oxidizing species, as discussed below, *i.e.* in this kind of system, DMSO acts as a prooxidant.[34]

## Experimental

Solutions of EDTA (ethylenediaminetetraacetic acid) and an OH-radical scavenger (*tert*-butyl alcohol, methanol, acetonitrile, acetamide, guanosine) were saturated with oxygen for about 20 min. An aliquot containing the desired quantity of dimethyl sulfoxide was then added. Finally an aliquot of a ferrous sulfate solution was mixed in such that at the start of the reaction, $[Fe^{2+}]$ was, *e.g.*, $1.5 \times 10^{-3}$ mol dm$^{-3}$, and [EDTA] $2 \times 10^{-3}$ mol dm$^{-3}$. For the duration of the reaction time, which was 15 min, oxygen was bubbled in, in order to avoid depletion. Experiments were carried out at pH 2.3 (adjusted with perchloric acid) and 7.0 (adjusted with NaOH). The complete oxidation to ferric ($\lambda_{max}$ 256 nm, $\varepsilon = 7500$ dm$^3$ mol$^{-1}$ cm$^{-1}$) was always assured.

Methanesulfinic acid was determined by ion chromatography (Dionex ionpac AS9-SC, eluent $5 \times 10^{-4}$ mol dm$^{-3}$ sodium bicarbonate), using a solution of authentic material at a known concentration obtained by the γ-radiolysis of an aqueous solution of dimethyl sulfoxide,[30] or of commercial sodium methanesulfinate (85%, Arcos), as a standard. Formic acid was also determined by ion chromatography (Dionex, conditions as above). Formaldehyde was determined spectrophotometrically by the acetylacetone method[35] (in the presence of iron(III), it is useful to analyze by HPLC on Nucleosil C18, eluent methanol–water 40:60, optical detection at 413 nm). Hydroperoxides including hydrogen peroxide, using an iodometric method[36] for detection, were absent from the products (less than $10^{-5}$ mol dm$^{-3}$). Suitable blanks were used in all of these analyses.

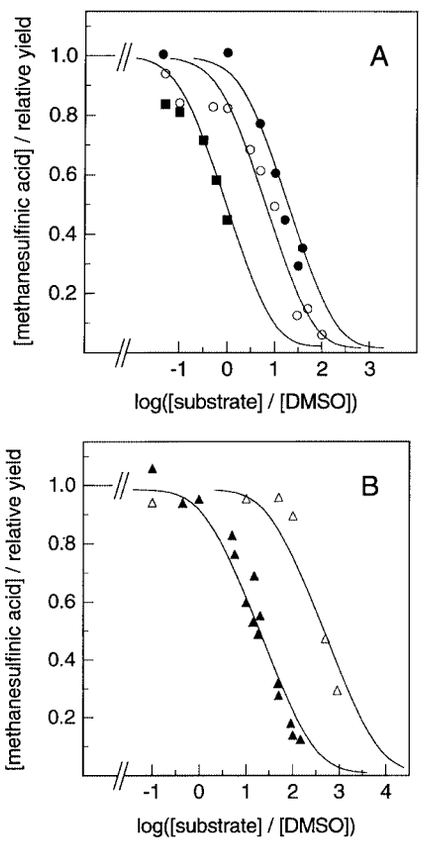


**Fig. 1** Formation of methanesulfinic acid in the system Fe(II)–EDTA–dioxygen–DMSO in the presence of various substrates. **A**: Guanosine (■), methanol (○), acetamide (●); **B**: *tert*-butyl alcohol (▲), acetonitrile (△).

## Results and discussion

### Competitive product formation

Oxygenated Fe(II)–EDTA solutions containing DMSO and a second substrate in varying proportions undergo autoxidation until all of the Fe(II) is converted to Fe(III). Under these conditions, methanesulfinic acid is produced in proportion to the initial concentration of Fe(II) (see below), its amount depending on the ratio of [DMSO]:[substrate] (Fig. 1).

It turns out that these results are adequately described under the assumption that it is the OH radical that is the attacking species (as would be expected, see below). In this case, at the half-value of methanesulfinic acid production, expression (13) holds.

$$k_{DMSO}[DMSO] = k_{substrate}[substrate] \quad (13)$$

Table 1 compares the experimental values of the ratio [substrate]:[DMSO] at half-maximal methanesulfinic acid with the ratio of the rate constants $k_{DMSO}:k_{substrate}$. It is apparent that there is reasonably good agreement between experiment and expectation.

There is further support for the contention that the OH radical is the attacking species. Certain metal–oxo complexes MO reacting with members of homologous series of C–H bond-containing compounds RH by hydrogen-atom abstraction have been shown (*cf*. ref. 37) to obey the Polanyi equation (14) which

$$E_{act} = \alpha + \beta\Delta H \quad (14)$$

under certain conditions provides an empirical correlation between the activation energy $E_{act}$ of an H-atom abstraction reaction and the difference $\Delta H$ between the bond strengths $D$(MO–H) and $D$(R–H) (*cf*. ref. 38). The parameters $\alpha$ and $\beta$

**Table 1** Experimental [*cf.* expression (13)] and literature values for the ratios $k_{DMSO}:k_{substrate}$ of rate constants

| Substrate | ([Substrate]/[DMSO])$_{1/2}$ | $k_{DMSO}:k_{substrate}$ (ref. 52) |
|---|---|---|
| Guanosine | 0.8 | 0.83 |
| Methanol | 6.7 | 6.8 |
| *tert*-Butyl alcohol | 19 | 11 |
| Acetamide | 20 | 34 |
| Acetonitrile | 490 | 300 |

are characteristic of a homologous series of reactions. The difference between the activation energies of two reactions superscripted ($p$) and ($q$) ($p$, $q$ referring to the substrates $R^{(p)}$–H and $R^{(q)}$–H) within a series ($i$) of homologous reactions (15) is given by expression (16).

$$A\ (B) + R^{(i)}H \longrightarrow AH\ (BH) + {}^{\bullet}R^{(i)} \quad (15)$$

$$(E_{act,p} - E_{act,q})_A = \beta^A\ (\Delta H_p - \Delta H_q) = \beta^A\ (D(R^{(p)}\text{–H}) - D(R^{(q)}\text{–H})) \quad (16)$$

Only if, for the H-abstractors A and B (which may or may not be free radicals, *cf*. ref. 37), the coefficients $\beta^A$ and $\beta^B$ are equal, will the differences of the activation energies $(E_{act,p} - E_{act,q})_A$ and $(E_{act,p} - E_{act,q})_B$, *i.e.* the ratios of rate constants $(k_p/k_q)_A$ and $(k_p/k_q)_B$, *also* be equal (assuming the ratio of the Arrhenius frequency factors to be unity in each case; obviously the value of the term $(D(R^{(p)}\text{–H}) - D(R^{(q)}\text{–H}))$ is independent of the nature of the abstractors A or B). This is not impossible but unlikely in the present case where the OH radical is strongly implicated, all of whose H-atom abstraction reactions are highly exothermic, *i.e.* $\beta^{OH}$ is very likely smaller than $\beta^{MO}$ since $E_{act}$ must always be positive. Moreover, the reactants chosen in the present experiments involve not only H-abstraction reactions but also reactions of a different type, *e.g.* addition reactions as far as the OH radical is concerned. The possibility that a metal–oxyl radical $MO^{\bullet}$ could mimic the OH radical with respect to each of the probe compounds used in this study, is very small indeed. All the data are therefore best explained on the basis of the OH radical being the reactive species, generated in Fenton-type processes from hydrogen peroxide. The formation of OH radicals in an *anoxic* EDTA–Fe(II)–$H_2O_2$ system has been confirmed recently.[26]

### Mechanism and stoichiometry of methanesulfinic acid formation

If one follows Seibig and van Eldik,[18] the initiation stage of the present autoxidation system consists of reactions (1)–(4), plus (9)–(12); the sequence of reactions (1), (2), and (5)–(8) gives the same stoichiometry as do reactions (1)–(4). Propagation is expected to involve mainly the methyl radical and its peroxyl descendants, in tandem with Fenton-type cleavage of the hydroperoxides (*cf*. ref. 39). The reaction chain is perhaps quite long as the rates of the reactions (18) and (22) of the peroxyl radicals with the ferrous complex, are competitive with their termination at these ferrous-complex concentrations (ref. 40 p. 259). Oxyl radicals such as the intermediate methoxyl and hydroxymethoxyl radicals have very short lifetimes with respect to rearrangement [reactions (20) and (24)] *via* a hydrogen 1,2-shift (*cf*. ref. 41–43) which prevents them from interacting with the ferrous complex. The dihydroxymethylperoxyl radical is known[44] to rapidly eliminate $HO_2^{\bullet}$, giving rise to formic acid [reaction (26)], in contrast with its predecessor peroxyls (*cf*. ref. 45). The reduction of $HO_2^{\bullet}$ to $H_2O_2$ [reactions (7) and (8)] leads up to the Fenton reaction (9)–(10) which closes the chain.

$$CH_3^{\bullet} + O_2 \longrightarrow CH_3OO^{\bullet} \quad (17)$$

$$CH_3OO^{\bullet} + L{\cdot}Fe^{2+} + H_2O \longrightarrow CH_3OOH + L{\cdot}Fe^{3+} + OH^- \quad (18)$$

$$CH_3OOH + L{\cdot}Fe^{2+} \longrightarrow CH_3O^{\bullet} + L{\cdot}Fe^{3+} + OH^- \quad (19)$$

$$CH_3O^{\bullet} \longrightarrow {}^{\bullet}CH_2OH \quad (20)$$

$${}^{\bullet}CH_2OH + O_2 \longrightarrow HOCH_2OO^{\bullet} \quad (21)$$

$$HOCH_2OO^{\bullet} + L{\cdot}Fe^{2+} + H_2O \longrightarrow HOCH_2OOH + L{\cdot}Fe^{3+} + OH^- \quad (22)$$

$$HOCH_2OOH + L{\cdot}Fe^{2+} + H_2O \longrightarrow HOCH_2O^{\bullet} + L{\cdot}Fe^{3+} + OH^- \quad (23)$$

$$HOCH_2O^{\bullet} \longrightarrow {}^{\bullet}CH(OH)_2 \quad (24)$$

$${}^{\bullet}CH(OH)_2 + O_2 \longrightarrow (HO)_2CHOO^{\bullet} \quad (25)$$

$$(HO)_2CHOO^{\bullet} \longrightarrow HCO_2H + HO_2^{\bullet}\ (O_2^{\bullet -} + H^+) \quad (26)$$

In this context it may be worth noting that generally such peroxyl-radical-driven processes contribute to the phenomenon of oxidative ligand destruction that has often been observed, in proportion to the ratio of the concentrations of ligand and substrate. Further, in the case of substrates that form reducing radicals, the peroxyl-radical pathway of autoxidation may lose its pre-eminence at relatively low oxygen concentrations as these radicals may be oxidized by the ferric species instead of $O_2$.[46]

As expected, formic acid is experimentally confirmed as a product of this autoxidation (Table 2). However, formaldehyde is observed as well. It is assumed that this is due to reaction (27). Hydroxymethylperoxyl is known to undergo a rapid *base-catalyzed* elimination of $O_2^{\bullet -}$ (*cf*. ref. 47). EDTA anion is assumed to act as the base in the present case. This hypothesis is supported by the observation that at the higher EDTA concentration the formaldehyde yield increases relative to the formic acid yield. Moreover, owing to the fact that the concentration of the species $LFe^{2+}$ decreases as the autoxidation progresses, the chemistry shifts away from the formation of formic acid [reactions (22)–(26)], in favour of the formation of formaldehyde [reaction (27)].

$$HOCH_2OO^{\bullet} + EDTA \longrightarrow CH_2O + O_2^{\bullet -} + EDTAH^+ \quad (27)$$

The nature of the terminating reactions, as well as the chain length, is not clear at this stage. Termination involves probably for the most part reactions of the type $ROO^{\bullet} + ROO^{\bullet} \longrightarrow$ products. In principle, the reduction of oxyl radical by the ferrous-ion complex represents a further route for free-radical removal; so could a reduction of the ferric complex by $O_2^{\bullet -}$ which is in equilibrium with $HO_2^{\bullet}$ [equilibrium (6)].[48] There is no information at present regarding the fate of the [minor, *ca*. 8%,[27] *cf*. reaction (12)] radical ${}^{\bullet}CH_2S(O)CH_3$. Insofar as the peroxidation and decay of this radical lead to a non-propagating radical, the length of the reaction chain would be correspondingly reduced.

The existence of a complex chain reaction in the Fe(II)–EDTA–$O_2$–DMSO system has wider implications. Fenton systems have sometimes been used under conditions of the non-exclusion of atmospheric oxygen. In particular, such Fenton systems have been used in studies on DNA (*cf*. ref. 49 and references therein) and its monomeric constituents (*cf*. ref. 50); differences between the outcome of such experiments and that caused by the action of the radiolytically-generated OH radical have been noted and discussed, usually, however, without taking into account the ramifications due to the interaction of the concomitant peroxyl radicals and hydroperoxides with the Fe(II) complex used.

The endpoint of the above experiments is characterized by

**Table 2** Initial reactant concentrations and pH. Product yields in terms of concentrations (in units of $10^{-3}$ mol $dm^{-3}$). Multiple entries in columns 5–7 give an impression of the degree of scatter in the results of these experiments

| [Fe(II)] | [EDTA] | [DMSO] | pH | $[CH_3SO_2H]$ | $[HCO_2H]$ | $[CH_2O]$ |
|---|---|---|---|---|---|---|
| 1.5 | 2 | 10 | 7.0 | 0.23/0.26/0.21/0.29/0.28/ 0.24/0.19 | 0.15/0.16/0.15/0.16/0.15/0.16 | 0.08/0.08/0.09/0.09 |
| | | | 2.3 | 0.20/0.20/0.19/0.18/0.24/0.23 | 0.26/0.25/0.21/0.19/0.25 | 0.06/0.07/0.06 |
| 1.5 | 2 | 100 | 7.0 | 0.26/0.27/0.16/0.18 | 0.15/0.16/0.14/0.15 | 0.08/0.08/0.09 |
| 15 | 20 | 100 | 7.0 | 3.1/2.6/3.0/3.2/1.8/1.9/3.1/2.8 | 0.38/0.26/0.55/0.55/0.25/0.40/ 0.31/0.35 | 0.50/0.47/0.52/0.42/ 0.41/0.41 |

the complete oxidation of ferrous to ferric. (As ferrous ion becomes depleted in the course of the autoxidation, the attainment of the endpoint is retarded on account of the reverse of reaction (8),[51] but this has no influence on the stoichiometry.) In the (hypothetical) absence of peroxyl radical formation, the ratio of methanesulfinic acid to ferric ion would be near 1 : 3. However, the results in Table 2 indicate that these products are formed in the ratio of between 1 : 5 and 1 : 6. This is in agreement with the foregoing mechanism which suggests that this ratio will incline toward the side of the smaller value when the oxidation of the methyl-radical fragment stops at $CH_2O$ instead of $HCO_2H$. Indeed, the highest values for methanesulfinic acid : Fe(III) are found where the ratio of $CH_2O : HCO_2H$ is largest, *i.e.* where the EDTA concentration is relatively large and the buffering effect comes more strongly into play (Table 2).

Finally it may be worth noting that, quite generally, in autoxidative systems such as the one investigated any participation of higher-valent iron–oxo species is almost certain to remain obscured by a dominance of free-radical chain processes mediated by the OH radical.

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