OH-Radical induced degradation of ethylenediaminetetraacetic acid (EDTA) in aqueous solution: a pulse radiolysis study

Bernd Höbel and Clemens von Sonntag *

Max-Planck-Institut für Strahlenchemie, Stiftstr. 34–36, PO Box 101365,
D-45413 Mülheim/Ruhr, Germany

Hydroxyl radicals have been generated pulse radiolytically in N_2O- and N_2O–O_2-saturated solutions. In their reaction with *N,N,N′,N′*-ethylenediaminetetraacetic acid (EDTA) they give rise to an absorption spectrum with maxima at 275 and 480 nm. The 480 nm band decays ($k = 3.3 \times 10^4$ s^{-1}) with a concomitant increase at around 290 nm. The 480 nm intermediate does not react with O_2 and has been attributed to an *N*-centered radical cation bridged to the second nitrogen ($N^{\bullet +}N$–EDTA). Using strong reductants as probes, *e.g. N,N,N′,N′*-tetramethylphenylenediamine, $G(N^{\bullet +}N\text{–EDTA}) = 1.6 \times 10^{-7}$ mol J^{-1} has been obtained. Besides generating $N^{\bullet +}N$–EDTA, the OH radicals produce *C*-centered radicals by H-abstraction. They have reducing properties and react rapidly with tetranitromethane forming the strongly absorbing nitroform (trinitromethane) anion [NF^-; $k = 10^9$ dm^3 mol^{-1} s^{-1}; $G(NF^-) = 4.2 \times 10^{-7}$ mol J^{-1}]. This rapid formation of NF^- is followed by a slower one [$G(NF^-) = 1.5 \times 10^{-7}$ mol J^{-1}] showing the same kinetics as the decay of the 480 nm absorption. It is hence concluded that the $N^{\bullet +}N$–EDTA species decays into reducing *C*-centered radicals by deprotonation or electron transfer from a carboxylate group. The *C*-centered radicals react rapidly ($k = 7.6 \times 10^8$ dm^3 mol^{-1} s^{-1}) with O_2, and subsequent fast $O_2^{\bullet -}$ elimination. The Schiff-bases thus formed hydrolyze yielding the final products.

In the presence of oxygen the following products (*G* values in units of 10^{-7} mol J^{-1} in parentheses) have been observed after γ-radiolysis: formaldehyde (1.6), CO_2 (2.5), formic acid (0.7), glyoxylic acid (3.6), iminodiacetic acid (2.1), ethylenediaminetriacetic acid (detected, not quantified).

Ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and diethylenetriaminepentaacetic acid (DTPA) are widely used as calcium complexing agents. While NTA is biodegraded reasonably well, EDTA is not. Hence, EDTA is often found as a water pollutant. Since EDTA also readily complexes other metal ions, *e.g.* transition metal ions that are required for the functioning of enzymes, its presence in drinking-water could be a potential risk to man, and its elimination is desirable. Oxidation of water pollutants by ozone is common usage in drinking-water processing, and EDTA is known to be degradable by ozone.[1,2] This reaction strongly depends on the pH of the solution, and we have found in work to be published elsewhere that EDTA reacts quickly with this oxidant only when it is unprotonated at nitrogen. In contrast, OH radicals react very rapidly with EDTA at all pH values relevant for drinking water.[3] There is an increasing interest in the use of OH-radical-generating systems (advanced oxidation processes) in drinking-water processing, *e.g.* a combination of ozone and hydrogen peroxide ($2\ O_3 + H_2O_2 \longrightarrow 2{\cdot}OH + 3\ O_2$; for a discussion of the primary processes see ref. 4). This raises the question of which products are formed from EDTA after OH-radical attack, and how they are formed.

It turns out that there is a great variety of products, and in the present study we have investigated mechanistic details using pulse radiolysis.

Experimental

Ethylenediaminetetraacetic acid (Fluka) was used as received; all other chemicals were of the highest purity commercially available. Aqueous solutions were made up in Milli-Q-filtered (Millipore) water. Oxygen-free N_2O and N_2O–O_2 (4 : 1) mixtures were obtained from Messer Griesheim.

For the pulse radiolytic experiments a 2.7 MeV Van de Graaf electron accelerator delivering 0.4 µs pulses was used.[5] The rate constant of the OH radical with EDTA at pH 11 has been determined by following the build-up at 260 nm. This wavelength is close to an isosbestic point, and hence a subsequent first-order transformation reaction does not interfere with the evaluation of the kinetics of the OH-radical reaction.

γ-Irradiation was carried out using a ^{60}Co-γ-source, mainly at a dose rate of 0.16 Gy s^{-1}. Formaldehyde has been determined by the acetylacetone method.[6] Iminodiacetic acid was derivitized with fluoren-9-ylmethyl chloroformate (FMOC) and detected by fluorimetry ($\lambda_{excit} = 260$ nm, $\lambda_{detect} = 315$ nm) after separation by HPLC [125 mm Nucleosil-C_{18} (Merck); eluent: 60% MeOH–40% H_2O–0.3% acetic acid, adjusted to pH 4.2]. Glyoxylic, glycolic and formic acids were determined by ion chromatography (Dionex DX-100; AS9-SG column, eluent: 5×10^{-4} mol dm^{-3} $NaHCO_3$). Carbon dioxide was determined by GC [Porapak Q (3.2 m) and by ion chromatography (AS1 column, eluent: water). In the presence of H_2O_2 glyoxylic acid decomposes into CO_2 and formic acid. In order to arrive at the initial yields of these acids irradiated samples (4.7 Gy s^{-1}, 1–4 min irradiation time) were reduced with $NaBH_4$ immediately following irradiation. Glycolic and formic acids were then quantified by ion chromatography. The consumption of EDTA was monitored by ion-pair chromatography with a UV detector at 254 nm {125 mm Nucleosil-C_{18} (Merck); eluent: 8 ml HNO_3 (1 mol dm^{-3}), 100 mg $Fe(NO_3)_3{\cdot}9H_2O$, 10 ml 5% aqueous $[Bu^t_4N]NO_3$ dissolved in 1000 ml of triply distilled water}.[7] The generation of formic acid, glyoxylic acid, iminodiacetic acid and ethylenediaminetriacetic acid, and the decomposition of EDTA were also measured by isotachophoresis (ItaChrom EA 101 Merck): leading electrolyte: 2×10^{-2} mol dm^{-3} L-histidine, 1×10^{-2} mol dm^{-3} HCl and 0.05% Triton-X-100; terminal electrolyte: 5×10^{-3} mol dm^{-3} L-histidine and 5×10^{-3} mol dm^{-3} 2-morpholinoethanesulfonic acid; current intensity: pre-column (160 mm, 0.8 mm i.d.) 250 µA, analytical column (90 mm, 0.3 mm i.d.) 50 µA. A compound coeluting with glyoxylic acid was attributed to ethylenediaminetriacetic acid. It was distinguished from glyoxylic acid by converting glyoxylic acid into formic acid with H_2O_2. The formation of glyoxylic acid, iminodiacetic acid and ethylenediaminetriacetic acid was confirmed as their

Table 1 Compilation of the rate constants determined in this study[a]

Reaction	Rate constant
$^{\bullet}OH + H_2EDTA^{2-} \longrightarrow$ EDTA radicals	4×10^8 dm^3 mol^{-1} s^{-1}
$^{\bullet}OH + HEDTA^{3-} \longrightarrow$ EDTA radicals	2×10^9 dm^3 mol^{-1} s^{-1}
$^{\bullet}OH + EDTA^{4-} \longrightarrow$ EDTA radicals	6×10^9 dm^3 mol^{-1} s^{-1}
N-centered EDTA radical cation $\longrightarrow$ *C*-centered radicals	3.3×10^4 s^{-1}
2*C*-centered EDTA radicals $\longrightarrow$ products (at pH 7)	$\approx 10^6$ dm^3 mol^{-1} s^{-1}
C-centered EDTA radicals + TNM $\longrightarrow$ products + NF$^-$	1×10^9 dm^3 mol^{-1} s^{-1}
C-centered EDTA radicals + $O_2 \longrightarrow$ EDTA preoxyl radicals	7.6×10^8 dm^3 mol^{-1} s^{-1}
EDTA preoxyl radicals $\longrightarrow$ products + $O_2^{\bullet -}$	$\geq 10^5$ s^{-1}

[a] TNM = tetranitromethane; NF$^-$ = nitroform (trinitromethane anion).

isopropyl esters by GC–MS.[8] The irradiated samples were rotary-evaporated to dryness and treated with acetyl chloride–propan-2-ol at 85 °C for 4 h. Under these reaction conditions ethylenediaminetriacetic acid largely cyclizes and is detected as ketopiperazinediisopropyl diacetate.[8]

Results and discussion

The radical-generating system

Hydroxyl radicals were generated radiolytically in N_2O-saturated aqueous solutions [reactions (1) and (2); $k_2 = 9.8 \times 10^9$ dm^3 mol^{-1} s^{-1}, *cf.* ref. 9]. The radiation-chemical yields of the primary radicals are $G(^{\bullet}OH) \approx G(e_{aq}^-) = 2.9 \times 10^{-7}$ mol J^{-1} and $G(^{\bullet}H) = 0.6 \times 10^{-7}$ mol J^{-1}. Solvated electrons are converted with N_2O into further OH radicals.[10] Hydroxyl radicals react rapidly with EDTA [reaction (3); *e.g.* $k_3 = 2 \times 10^9$ dm^3 mol^{-1} s^{-1}, see below], and the H atom also reacts with EDTA reasonably fast, albeit with a lower rate constant ($k = 6 \times 10^7$ dm^3 mol^{-1} s^{-1} at pH 1).[3]

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} {}^{\bullet}OH,\ e_{aq}^-,\ H^{\bullet},\ H^+,\ OH^-,\ H_2,\ H_2O_2 \qquad (1)$$

$$e_{aq}^- + N_2O \longrightarrow {}^{\bullet}OH + N_2 + OH^- \qquad (2)$$

$$^{\bullet}OH + \text{EDTA} \longrightarrow \text{EDTA-derived radicals} \qquad (3)$$

In the presence of O_2 (solutions saturated with a 4 : 1 mixture of N_2O and O_2), the OH radicals formed in reactions (1) and (2) still react with EDTA, but the H atoms are converted into $HO_2^{\bullet}$ and $O_2^{\bullet -}$ radicals [reaction (4); $k_4 = 1.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}; p$K_a(HO_2^{\bullet}) = 4.8$; *cf.* equilibrium (5)].[11]

$$H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet} \qquad (4)$$

$$HO_2^{\bullet} \rightleftharpoons H^+ + O_2^{\bullet -} \qquad (5)$$

Deoxygenated solutions

Depending on pH, EDTA is present in several different protonation states. Denoting the neutral EDTA molecule as H_4EDTA its six pK_a values are 0.26 (H_6EDTA^{2+}), 0.96 (H_5EDTA^+), 2.0 (H_4EDTA), 2.7 (H_3EDTA^-), 6.2 (H_2EDTA^{2-}) and 10.3 ($HEDTA^{3-}$).[12] The OH radical is electrophilic in its reactions with acids, and more strongly with amines; its rate of reaction is reduced when the substrate is protonated (*cf.* data compiled in ref. 9). Thus, at pH 4, OH radicals react with EDTA (H_2EDTA^{2-}) with a rate constant of $k_3 = 4 \times 10^8$ dm^3 mol^{-1} s^{-1} and much faster at pH 9 ($HEDTA^{3-}$; $k_3 = 2 \times 10^9$ dm^3 mol^{-1} s^{-1}).[3] Our own data agree with these values (for a compilation of rate constants determined in this study see Table 1). At pH 11, where $EDTA^{4-}$ dominates, we have determined the rate constant pulse radiolytically by following the build-up of the absorption of EDTA-derived radicals at 260 nm [close to an isosbestic point (see below)] and found that it further increases to a value of $k_3 = 6 \times 10^9$ dm^3 mol^{-1} s^{-1}. It is not yet known, exactly to what extent the nitrogen atoms are protonated in the zwitterions. However, these data clearly show that a deprotonation of at least one nitrogen is required for the reaction to become close to diffusion-controlled.

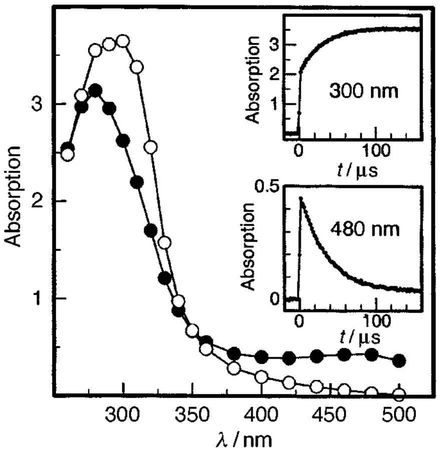


Fig. 1 Pulse radiolysis of N_2O-saturated solutions of EDTA at pH 7; ●, immediately after the pulse, ○ 140 µs after the pulse. Insets: build-up kinetics at 300 and decay kinetics at 480 nm.

When N_2O-saturated solutions of EDTA (10^{-3} mol dm^{-3}) are pulse-irradiated at pH 7 a spectrum characterised by absorption maxima at 280 nm and 480 nm is obtained (Fig. 1; *cf.* also ref. 3).

While the band at 480 nm decays, a build-up at 300 nm is observed. In both cases the kinetics were of first order ($k = 3.3 \times 10^4$ s^{-1}) at low doses per pulse (6–8 Gy) and are the same for these two wavelengths. There is an isosbestic point at 260–270 nm. The absorption at this wavelength decays by second-order. At a dose of 8 Gy only 30% of the radicals had decayed after 100 ms. Thus the bimolecular termination rate constant must be of the order of $2k \approx 10^6$ dm^3 mol^{-1} s^{-1}. It is known that the pK_a values of acids do not change very much when an α-hydrogen is abstracted.[13,14] Thus at pH 7 the EDTA-derived radicals are most likely triply negatively charged, and the slowness of their bimolecular decay will be largely due to electrostatic repulsion (*cf.* ref. 15).

Tetranitromethane (TNM) can be used to probe reducing radicals [reaction (6)] by following the formation of the nitroform anion which absorbs strongly at 350 nm (ε 15 000 dm^3 mol^{-1} cm^{-1}).[16]

$$^{\bullet}RH\ (\text{reducing}) + C(NO_2)_4 \longrightarrow R + C(NO_2)_3^- + H^+ + {}^{\bullet}NO_2 \qquad (6)$$

In the presence of TNM nitroform anions are formed with a total G value of 6.3×10^{-7} mol J^{-1}. The build-up is biphasic (Fig. 2) consisting of a fast part the rate of which depends on the TNM concentration [$G(NF^-) = 4.9 \times 10^{-7}$ mol J^{-1}; $k = 1 \times 10^9$ dm^3 mol^{-1} s^{-1}, *cf.* inset in Fig. 2] and a slow part [$G(NF^-) = 1.4 \times 10^{-7}$ mol J^{-1}]. The rate constant of the latter is only monitored well at TNM concentrations above 10^{-4} mol

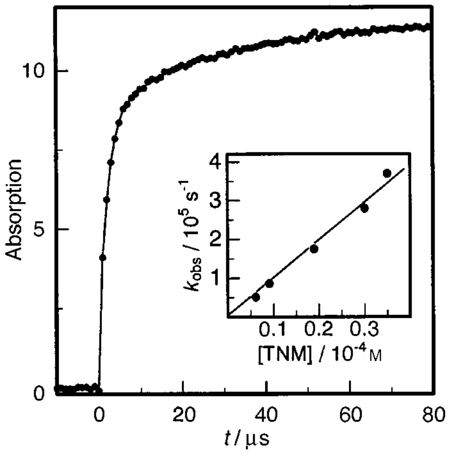


Fig. 2 Pulse radiolysis of N_2O-saturated solutions of EDTA at pH 7 in the presence of 3.5×10^{-4} mol dm^{-3} tetranitromethane. Inset: rate of the fast part of the build-up as a function of the tetranitromethane concentration.

dm^{-3}; in this range it does not depend on the TNM concentration and its rate is *ca.* 3.5×10^4 s^{-1}.

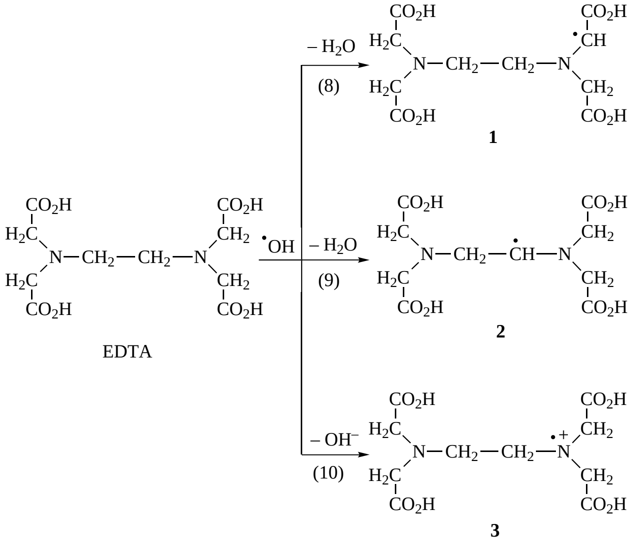
The fast component will comprise the H atoms which react more quickly with TNM ($k = 2.6 \times 10^9$ dm^3 mol^{-1} s^{-1})[9] than with EDTA (see above). From these data it is concluded that upon OH radical attack two kinds of radicals are formed: reducing ones which react very fast with TNM (75%) and non-reducing ('oxidizing') ones (25%) which do not react with TNM. The fact that the second and slow build-up of NF^- formation is independent of the TNM concentrations shows that we do not deal with a more slowly reacting primary 'reducing' radical, but that a primary 'oxidizing' radical decays unimolecularly into a 'reducing' one. From the TNM experiments a decay rate of 3.5×10^4 s^{-1} is obtained. Practically the same rate constant has been found for the decay of the 480 nm band (in the absence of TNM), and it is hence concluded that this absorption must be due to the 'oxidizing' radical.

The formation of oxidizing radicals in this system can be monitored with 2,2′-azino-(3-ethyl-2,3-dihydrobenzothiazole-6-sulfonate) (ABTS) at pH 3–6 and with *N*,*N*,*N*′,*N*′-tetramethylphenylenediamine (TMPD) at pH 7–9 [*e.g.* reaction (7)].

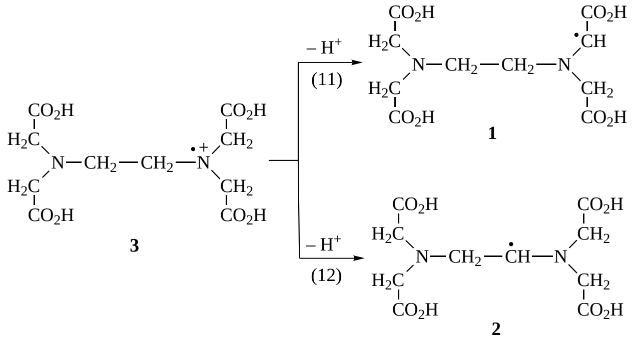
$$^{\bullet}\mathrm{RH}\ (\text{oxidizing}) + \mathrm{H_2O} + \mathrm{TMPD} \longrightarrow \mathrm{RH_2} + \mathrm{TMPD}^{\bullet+} + \mathrm{OH^-} \quad (7)$$

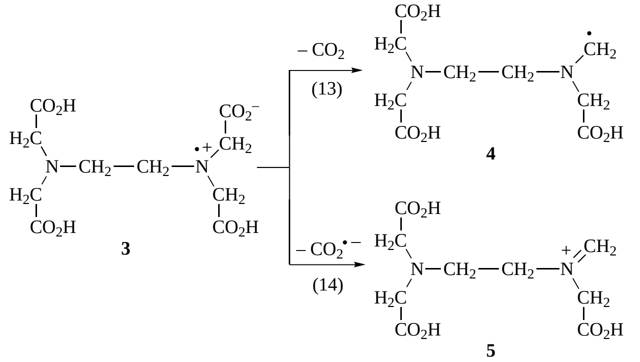
The absorption coefficients of the ABTS radical cation [ε (415 nm) 26 000 dm^3 mol^{-1} cm^{-1}][17] and the TMPD radical cation [ε (565 nm) 12 500 dm^3 mol^{-1} cm^{-1}][18] are known and from the final absorption values *G*(oxidizing radicals) = 1.5×10^{-7} mol J^{-1} is calculated, a value which agrees well with the TNM data given above.

In reactions (8) and (9) radicals are formed (**1** and **2**), where the radical site is at a carbon carrying nitrogen in the α-position (for reasons of clarity in these and other reactions EDTA is only shown in its neutral form). They have hence reducing properties. In the free-radical chemistry of amines (*e.g.* trimethylamine)[19] it has also been recognised that oxidizing radicals are formed by OH radical attack. They have been attributed to *N*-centered radical cations [*cf.* radical **3**, reaction (10)]. The pronounced absorption at 480 nm is attributed to an *N*-centered radical cation. The radical cation derived from trimethylamine is characterised by a shoulder at 360 nm.[19] Thus there is a considerable shift to longer wavelengths in the present system. We suggest that this shift is due to a complexation with the other amino group yielding a three-electron-bonded intermediate (*cf.* similar intermediates in sulfur free-radical chemistry[10,20,21]). The *N*-centered radical cation derived from 1,4-diazabicyclo[2.2.2]octane (DABCO) is of the same type as confirmed by EPR.[22] Its absorption maximum is, at 460 nm,[23,24] very close to the maximum of the EDTA-derived radical cation. In agreement with this assignment, nitrilotriacetic acid (NTA) which would give rise to an *N*-centered radical cation involving only one nitrogen does not give rise to the long-wavelength absorption (details to be published). It is noted that in order to allow such a bridging the second nitrogen must deprotonate. There is an analogy with DABCO, where its *N*–*N*-bridged radical cation is also observed in a pH range where DABCO itself is present as its monoprotonated form (details to be published).



Also in the case of the trimethylamine-derived radical cations a deprotonation into a reducing radical occurs.[19] In the present system the *N*-centered radical cations may convert into reducing radicals (**1** and **2**) by either deprotonating in the α-position [reactions (11) and (12)] or by electron transfer from one of the carboxylate groups [formation of radical **4**, reaction (13)]. A fragmentation according to reaction (14) would yield the $CO_2^{\bullet-}$ radical which is also reducing. A decision to the extent of the various possible pathways can only be made on the basis of a product study which will be presented below.





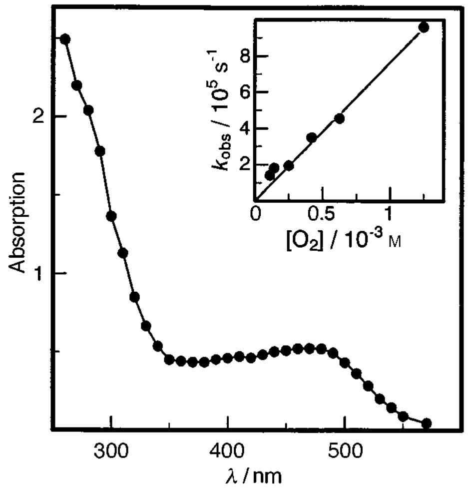


Fig. 3 Pulse radiolysis of N_2O–O_2 (1 : 1) saturated solutions of EDTA at pH 7. Spectrum after 8.6 µs. Inset: pulse radiolysis of N_2O–O_2 saturated solutions of EDTA at pH 7. Rate of decay of the absorption at 300 nm as a function of the O_2 concentration.

At pH 10.6 the spectrum is similar to that obtained at pH 7, and also the decay and build-up kinetics are the same (build-up at 300 nm: $k = 3.2 \times 10^4\ s^{-1}$, decay at 480 nm: $k = 3.3 \times 10^4\ s^{-1}$). Obviously, at this pH the OH^- concentration is not yet high enough to speed-up the transformation reaction, *i.e.* the OH^--induced deprotonation of the *N*-centered radical cation must be much lower than $8 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$. Deprotonations by OH^- at carbon are much slower than deprotonations at a heteroatom; the latter are usually close to diffusion controlled.

Oxygenated solutions

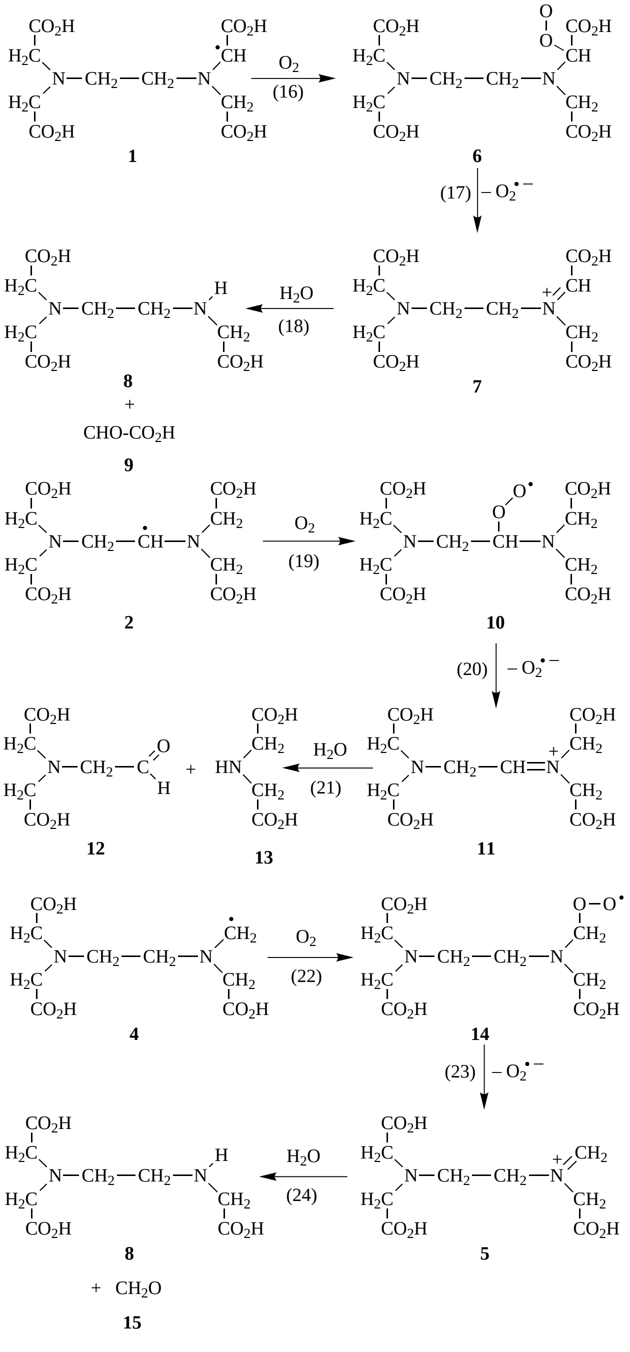
The absorption at 300 nm rapidly decays in the presence of O_2, while the decay at 480 nm is practically unaffected by O_2 (*cf.* Fig. 3). The latter observation further supports our assignment of the 480 nm absorption as being due to an *N*-centered radical cation **3**. The major part of the strong absorption at around 300 nm is hence attributed to the absorptions of the reducing radicals **1** and **2**. These radicals react easily with O_2 and from the data shown in the inset of Fig. 3, the rate constant $k = 7.6 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ is calculated.

The spectrum shown in Fig. 3 was obtained at elevated O_2 concentrations [N_2O–O_2 (1 : 1) saturated solutions] in order to speed-up the rate of the reaction with O_2. Under these conditions N_2O still scavenges the majority of solvated electrons, but some 20% are scavenged by O_2 [$k(e_{aq}^- + O_2) = 1.9 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$][9] yielding the superoxide radical, $O_2^{\bullet -}$. In these early times the *N*-centered radical cation **3** has not yet decayed to a noticeable extent, but the carbon-centered radicals **1** and **2** are converted into the corresponding peroxyl radicals. With a few exceptions[25,26] peroxyl radicals only absorb in the UV[27] as does $O_2^{\bullet -}$ (*cf.* ref. 11). Thus they are not expected to contribute to the long-wavelength absorption which must be entirely due to the *N*-centered radical cation **3**.

With the exception of the (reducing) superoxide radical, $O_2^{\bullet -}$, peroxyl radicals have oxidizing properties and do not react with TNM. This allows one to monitor the formation of $O_2^{\bullet -}$ in oxygenated solutions by its fast reaction with TNM [reaction (15), $k_{15} = 2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$].[16]

$$O_2^{\bullet -} + C(NO_2)_4 \longrightarrow O_2 + C(NO_2)_3^- + {}^{\bullet}NO_2 \quad (15)$$

In N_2–O_2 (4 : 1) saturated EDTA solutions at pH 7 and in the presence of TNM ($5 \times 10^{-5}\ mol\ dm^{-3}$) nitroform anions are formed with a final *G* value of *ca.* $5.7 \times 10^{-7}\ mol\ J^{-1}$ after ~100 µs. When experiments were carried out at the low dose rates of ^{60}Co γ-radiolysis a very similar value was obtained ($6.2 \times 10^{-7}\ mol\ J^{-1}$). Thus, all radicals are eventually converted into the reducing $O_2^{\bullet -}$ radicals. In the case of the reaction of O_2 with the trimethylamine-derived radical $^{\bullet}CH_2N(CH_3)_2$ no intermediate peroxyl radical could be detected, because the ensuing $O_2^{\bullet -}$-elimination is so fast [$^{\bullet}O_2$–$CH_2N(CH_3)_2 \longrightarrow O_2^{\bullet -} + {}^+CH_2{=}N(CH_3)_2$; $k > 10^6\ s^{-1}$].[28] In the present system the same type of reaction must occur [reactions (17), (20) and (23)], but it is difficult to assess exactly the rate of $O_2^{\bullet -}$-elimination. The TNM concentration must be kept low ($5 \times 10^{-5}\ mol\ dm^{-3}$) to avoid its unwanted competition with O_2 for the reducing radicals. In addition, further reducing radicals are formed in the decay of the *N*-centered radical cation ($k = 3.3 \times 10^4\ s^{-1}$). From the early part of the formation of nitroform anions under these conditions one estimates that the superoxide release should be faster than $10^5\ s^{-1}$.



The products which are formed in reactions (16, 17), (19, 20) and (22, 23) are tertiary iminium Schiff-bases which hydrolyse in water into aldehydes and secondary amines. The hydrolysis of these Schiff-bases must be fast, since a reduction with $NaBH_4$ which usually allows one to reduce Schiff-bases has no effect on the yields of the products in the present system.

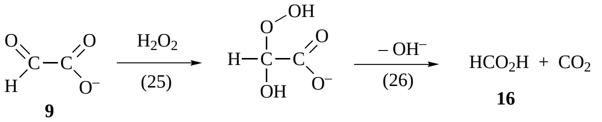
Table 2 γ-Radiolysis of EDTA (2×10^{-3} mol dm^{-3}) in N_2O-saturated and N_2O–O_2-saturated aqueous solutions. Products and their *G* values (in units of 10^{-7} mol J^{-1}). The yields of ethylenediaminetriacetic acid could not yet be quantified.

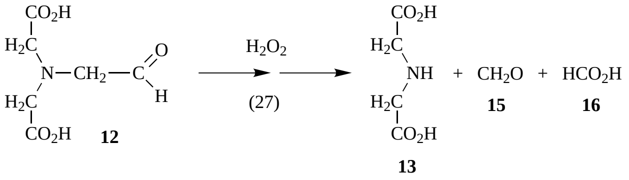
Product	N_2O	N_2O–O_2
Formaldehyde	0.2	1.6
Carbon dioxide	3.4	2.5
Formic acid	absent	0.7
Glyoxylic acid	0.5	3.6
Iminodiacetic acid	1.3	2.1
Ethylenediaminetriacetic acid	not determined	present
EDTA consumption	5.4	5.4

Preliminary product study

It has been shown above that the *N*-centered radical cation is converted into reducing *C*-centered radicals and that in the presence of oxygen all *C*-centered radicals are converted into Schiff-bases (**5**, **7** and **11**) and $O_2^{\cdot -}$. They will hydrolyse into ethylenediaminetriacetic acid **8** and glycolic acid **9** or formaldehyde **15** [reactions (18) and (24)] and iminodiacetic acid **13** and the aldehyde **12** [reaction (21)].

A product study has been undertaken (Table 2), but it must remain preliminary since an important product, ethylenediaminetriacetic acid **8**, although identified by GC–MS, could not be quantified reliably as yet. In addition, the quantification of glyoxylic acid and formic acid is not straightforward, because in the presence of hydrogen peroxide glyoxylic acid is quite rapidly decomposed into formic acid and carbon dioxide [reactions (25) and (26)].[29]





Furthermore, the *bonafide* product **12** escaped detection by GC–MS (also the corresponding alcohol that should have been formed after $NaBH_4$ reduction), and its decomposition according to reaction (27) [in analogy to reactions (25) and (26)] must remain a suggestion. Thus, a full material balance which would be required to distinguish between different pathways is still missing. However, the formaldehyde data given in Table 2 allow some mechanistic conclusions to be drawn.

In the absence of O_2 practically no formaldehyde is formed. This has to be taken as an indication that the fragmentation reaction (14) is of no importance. A conceivable β-fragmentation of the *N*-centered radical cation (not shown in the schemes) can also be neglected on the same basis.

Acknowledgements

This work was initiated and partially financed by the German Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie, Project 02WT9583.

References

1 E. Gilbert and S. Hoffmann-Glewe, *Water Res.*, 1990, **24**, 39.
2 E. Gilbert and M. Beyerle, *J. Water Supply Res. Technol.-Aqua.*, 1992, **41**, 269.
3 J. Lati and D. Meyerstein, *J. Chem. Soc.*, *Dalton Trans.*, 1978, 1105.
4 C. von Sonntag, G. Mark, R. Mertens, M. N. Schuchmann and H.-P. Schuchmann, *J. Water Supply Res. Technol. -Aqua.*, 1993, **42**, 201.
5 C. von Sonntag and H.-P. Schuchmann, *Methods Enzymol.*, 1994, **233**, 3.
6 T. Nash, *Biochem. J.*, 1953, **55**, 416.
7 W. Huber, *Acta Hydrochim. Hydrobiol.*, 1992, **20**, 6.
8 T. A. Ternes, M. Stumpf, T. Steinbrecher, G. Brenner and K. Haberer, *Vom Wasser.*, 1996, **87**, 275.
9 G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data.*, 1988, **17**, 513.
10 C. von Sonntag, *The Chemical Basis of Radiation Biology*, Taylor and Francis, London, 1987.
11 B. H. J. Bielski, D. E. Cabelli, R. L. Arudi and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1985, **14**, 1041.
12 E. P. Serjeant and B. Dempsey, *Ionisation constants of organic acids in aqueous solution*, Pergamon Press, Oxford, 1979.
13 P. Neta, M. Simic and E. Hayon, *J. Phys. Chem.*, 1969, **73**, 4207.
14 M. N. Schuchmann, H.-P. Schuchmann and C. von Sonntag, *J. Phys. Chem.*, 1989, **93**, 5320.
15 P. Ulanski, E. Bothe, K. Hildenbrand, C. von Sonntag and J. M. Rosiak, *Nucleonika*, 1997, **42**, 425.
16 K.-D. Asmus, A. Henglein, M. Ebert and J. P. Keene, *Ber. Bunsenges. Phys. Chem.*, 1964, **68**, 657.
17 B. S. Wolfenden and R. L. Willson, *J. Chem. Soc.*, *Perkin Trans. 2*, 1982, 805.
18 S. Fujita and S. Steenken, *J. Am. Chem. Soc.*, 1981, **103**, 2540.
19 S. Das and C. von Sonntag, *Z. Naturforsch. Teil B*, 1986, **41**, 505.
20 K.-D. Asmus, *Acc. Chem. Res.*, 1979, **12**, 436.
21 C. von Sonntag and H.-P. Schuchmann, in *The Chemistry of Functional Groups. The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues. Part 2*, ed. S. Patai, New York, Wiley, 1980, p. 971.
22 B. Samuelsson, *J. Am. Chem. Soc.*, 1965, **87**, 3013.
23 R. F. Anderson and K. B. Patel, *Photochem. Photobiol.*, 1978, **28**, 881.
24 J. E. Packer, J. S. Mahood, V. O. Mora-Arellano, T. F. Slater, R. L. Willson and B. S. Wolfenden, *Biochem. Biophys. Res. Commun.*, 1981, **98**, 901.
25 R. Mertens and C. von Sonntag, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1262.
26 X. Fang, R. Mertens and C. von Sonntag, *J. Chem. Soc.*, *Perkin Trans. 2*, 1995, 1033.
27 C. von Sonntag and H.-P. Schuchmann, in *Peroxyl Radicals*, ed. Z. B. Alfassi, London, Wiley, 1997, p. 173.
28 S. Das, M. N. Schuchmann, H.-P. Schuchmann and C. von Sonntag, *Chem. Ber.*, 1987, **120**, 319.
29 J. Etzel, Doctoral thesis, Universität Karlsruhe (TH); Report KfK 5176, 1993.

Paper 7/08167G
Received 12*th November* 1997
Accepted 21*st November* 1997